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PREPARED IN THE OFFICE OF
THE CHIEF OF ORDNANCE

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WAR DEPARTMENT,
WASHINGTON, *August 14, 1919.*

The following publication, entitled "Military Explosives," is published for the information and guidance of all concerned.

[461.1, A. G. O.]

BY ORDER OF THE SECRETARY OF WAR:

PEYTON C. MARCH,
General, Chief of Staff.

OFFICIAL:

P. C. HARRIS,
The Adjutant General.

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PREFACE.

This publication has been prepared by the Explosives Section, Ammunition Division, Ordnance Department, United States Army, for use of the Ordnance Department in the instruction of student officers.

A large portion of the original manuscript was prepared by Capt. John A. Marshall, Ordnance Department, but it has been considerably enlarged and revised by Lieut. Col. C. G. Storm, Ordnance Department. Acknowledgment is also made of the assistance of Maj. J. Herbert Hunter, Ordnance Department; Capt. C. A. Tibbals, jr., Ordnance Department; and Lieut. J. E. Woods, Ordnance Department, in connection with the preparation and revision of the text.

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QUESTIONS ON THE TEXT OF "MILITARY EXPLOSIVES."

INTRODUCTION.

1. Differentiate between the term explosives and high explosive.
2. Enumerate the phenomena occurring in sequence when a substance is exploded.
3. Define detonation.
4. Enumerate the three general divisions noted into which military explosives fall.
5. Define propellant.
6. Give the distinguishing characteristics between a propellant and high explosive with examples of each.
7. What criteria are used in selecting or rejecting a new substance for use as an explosive?
8. Are high explosives ever used alone or in combination with other substances to constitute a propellant? If so, when?
9. In general, what are the types of chemical reactions which are involved in the decomposition of an explosive?
10. What function does a high explosive serve?

CHAPTER I.

1. Discuss briefly the historical development of nitro cotton.
2. What differentiates nitro cotton from smokeless powder.
3. Discuss from the physical and chemical standpoint the term smokeless powder.
4. Define the phrase granulation of smokeless powder.
5. Discuss the various types of granulation of smokeless powder.
6. Classify the different processes involved in the manufacture of smokeless powder.
7. What is pyro cotton?
8. Differentiate between pyro cotton and smokeless powder.
9. What is the necessity of purifying raw cotton.
10. Describe the picking operation.
11. What would be the effect of nitrating cotton having a higher water content than that given by specifications:
    (*a*) Upon the cotton?
    (*b*) Upon the acid?
12. What are the points of difference and of similarity between the Thompson displacement system and the Du Pont dipper process?

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13. Describe in detail the Du Pont mechanical dipper process.

14. Describe in detail the Thompson displacement system of nitration.

15. What degree of nitration is attained in the ordinary manufacture of pyro cotton? Indicate the nearest empirical formula.

16. What considerations enter into the purification of pyro cotton?

17. How are these processes classified? Describe each in detail.

18. Discuss the Jordan engine.

19. What considerations limit the operation of the Tolhurst wringer?

20. Define dehydration. What chemical principles are involved in this procedure?

21. Discuss the operation of dehydration in detail.

22. What is a stabilizer? Where and why and how is it used?

23. Discuss the formation of the colloid, enumerating the several stages involved.

24. Indicate in a general manner by diagram the method used in forming a grain of powder from the finished colloid.

25. Define the term solvent recovery. Describe two different methods of accomplishing this operation.

26. Discuss the air drying of powder.

27. Does all powder receive air-dry treatment? If so, why?

28. What do you understand by the terms water dry and alcohol dry?

29. Describe the method of operation of a continuous drier.

30. What do you understand by blending of powder? Describe its principles and practice.

Chapter II.

1. Define the following terms:

Explosion.
Detonation.
Propellant.
Ignition.
Kinetic energy.
Granulation of powder.

2. What considerations govern the granulation of a raw powder grain?

3. Enumerate and describe briefly the different shapes of granulation.

4. What considerations determine the size of a powder grain? Discuss each.

5. Discuss the relationship of the different methods of drying to ballistics and stability of smokeless powder.

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6. What is meant by web average? Web inner? Web outer?

7. Should the green dimension of powder correspond to the die dimension? Discuss fully.

8. What considerations influence the calculation of web measurements?

9. What is the basis of calculation for all the dimensions of the dried powder grain?

10. Describe the method of measuring green powder.

11. Discuss stability of smokeless powder from the standpoint of storage.

12. Discuss the stability of smokeless powder from the standpoint of heat test, and from other general chemical view points.

13. What is reworked powder?

14. Indicate which of the following powders you would rework and why:

12-inch gun manufactured prior to 1908.
6-inch gun manufactured in 1910.
0.30 caliber manufactured in 1909.
12-inch mortar manufactured in 1914.
Bull's-eye powder manufactured in 1910.

15. What special considerations should be given the first two powders mentioned in the above question?

16. What processes of manufacture are concerned in the reworking of smokeless powder?

17. Indicate which of the processes are concerned:

(*a*) Drying.
(*b*) Nitrating.
(*c*) Boiling tub.
(*d*) Pulping.
(*e*) Screening.

18. Describe the process of manufacture of reworked powder.

19. Discuss its points of similarity and difference with the manufacture of straight smokeless powder.

20. What are your ideas relative to the stability of finished reworked powder?

21. Define the term explosion?

22. Differentiate between ignition, combustion, detonation, incendition.

23. Differentiate between single and multiperforated grains, discussing the web dimensions in each case.

24. Describe the Walsh grain.

25. What allowances must be made for shrinkage in determining die dimensions?

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26. Show the differences and similarities between green dimensions, die dimensions, and dry dimensions.

27. Give the formula for arriving at the determination of large "D."

28. Upon what factors is the average web of the die dependent?

29. Discuss the failure of a lot of powder to pass the ballistic test. Assume that the powder develops an excessive pressure, state your recommendations as to what procedure shall be followed: (*a*) On the same lot of powder; (*b*) upon the calculation of die dimensions for a new lot of powder for use in the same type of gun.

CHAPTER III.

1. Discuss the term stability of smokeless powder.

2. What is meant by stabilizer?

3. What is meant by an indicator?

4. Why is it necessary to rework powder?

5. What additional manufacturing processes are employed to rework smokeless powder?

6. Which ones are omitted?

7. What considerations govern the selection of a site for storage magazines?

8. Discuss the problems connected with fire protection in relation to the storage of smokeless powder.

9. How is smokeless powder stored?

10. What precautions would you observe in the hiring of labor for work around powder magazines?

11. Discuss the use of nonsparking tools.

CHAPTER IV.

1. What analyses are made upon raw materials entering into the manufacture of smokeless powder?

2. What control tests are made during the manufacture of smokeless powder?

3. What is meant by the term moisture and volatiles?

4. Do you differentiate between moisture and volatiles and total volatiles?

5. Enumerate the physical tests which are made on smokeless powder.

6. What raw materials are tested in smokeless powder manufacture?

7. Discuss in detail the tests made on any two raw materials.

8. Describe the method of making a test for ether-alcohol insoluble material in nitrocellulose.

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9. Describe the heat test at 65.5° C.
10. What is meant by degree of fineness?
11. Describe the 135° test.
12. Describe the method of making a determination for per cent nitrogen in nitrocellulose.
13. How would you make a determination for ash in smokeless powder?
14. Describe the method of making moisture and volatile tests on smokeless powder.
15. What manufacturing processes are concerned with the following tests?
    (*a*) Moisture and volatile.
    (*b*) Degree of fineness.
    (*c*) K. I. test for nitrocellulose.
    (*d*) Determination of moisture content in raw cotton.
16. How is powder stored? Describe the type of container used and discuss the salient points.
17. How may smokeless powder be properly stored in magazines?
18. Discuss the topography of the country where magazines may be erected.
19. Enumerate in detail what rules are to be observed in the storage of smokeless powder and high explosives.

Chapter V.

1. What is meant by the term compound propellants?
2. Describe infallible powder, its use and manufacture.
3. What is E. C. powder?
4. Give a brief historical summary of black powder.
5. Describe the manufacture of black powder.
6. What tests are made on finished black powder?
7. Describe any two tests.
8. Discuss the storage of black powder.
9. Enumerate the different grades of black powder.
10. Discuss the uses of any two grades.

Chapter VI.

1. When was black powder first used as a military explosive?
2. When was black powder displaced as a propellant powder?
3. Give present military uses of black powder.
4. Give composition of black powder.
5. Describe briefly method of manufacture.
6. In what grade of powder is hardwood charcoal used?
7. Give method for determination of sulphur.

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8. Give method for determination of chlorides, chlorates, and perchlorates.

9. Describe determination of specific gravity.

10. Give necessary precautions for storage and handling of black powder.

CHAPTER VII.

1. What is T. N. T.?

2. How would you use it? (*a*) As a bursting charge, (*b*) in combination with mercury fulminate?

3. What grades of T. N. T. are specified and how do they differ from each other?

4. What are the uses of each grade?

5. Describe the nitration processes involved.

6. How may T. N. T. be purified?

7. What criterion is used to determine purity during the manufacture of T. N. T.? Describe the test involved.

8. How would you make a determination of ash on T. N. T.?

9. Discuss the storage of T. N. T.

10. Discuss T. N. T. poisoning.

11. Describe the method of making the fineness test.

CHAPTER VIII.

1. Define ammonium picrate.

2. For what purposes is ammonium picrate used?

3. Discuss the hygroscopicity of ammonium picrate as compared with other explosives.

4. Describe the manufacture of ammonium picrate.

5. What details of manufacture must be carefully observed to secure reddish crystals?

6. How may ammonium picrate be reworked?

7. Can you make a melting point determination of ammonium picrate? How?

8. Describe briefly the determination of ammoniacal nitrogen.

9. How is free ammonia determined quantitatively in ammonium picrate?

10. Discuss briefly the storage of ammonium picrate.

CHAPTER IX.

1. Discuss the uses of picric acid.

2. Discuss its advantages and disadvantages for use as a high explosive.

3. How may some of these disadvantages be overcome?

4. Describe the process of sulphonation, as practiced in the manufacture of picric acid.

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5. Discuss briefly the chlorbenzol process of manufacture.
6. Discuss the physiological effect of picric acid upon the workmen.
7. Describe the method of making a solidification point determination on picric acid.
8. Describe the method of making an ash determination on picric acid.
9. Why is the presence of soluble lead in picric acid objectionable?
10. Discuss briefly the storage of picric acid.

CHAPTER X.

1. What is the difference between "nitrostarch" and "nitrostarch explosives"?
2. Give reasons for the adoption of nitrostarch explosives by the Ordnance Department.
3. What starch gives best results in manufacture of nitrostarch?
4. Describe briefly methods of manufacture of nitrostarch.
5. Give reasons for the use of oil in nitrostarch explosives.
6. Compare sensitiveness with other military explosives.
7. Give reasons for stability and instability.
8. What precautions are necessary in the storing and handling of nitrostarch and nitrostarch explosives?
9. State determination necessary in analysis of grenade powder.

CHAPTER XI.

1. Give chemical name for tetryl.
2. Give briefly method of manufacture.
3. State military uses.
4. Give relative strength or power as an explosive.
5. Give relative sensitiveness.
6. Give method for determination of sodium salts.
7. Give precautions necessary for handling and storage.

CHAPTER XII.

1. What is T. N. A.?
2. Discuss briefly method of manufacture.
3. Discuss toxic effects of T. N. A. manufacture.
4. Compare T. N. A. with tetryl and T. N. T. as to—
   (*a*) Stability.
   (*b*) Sensitiveness.
   (*c*) Explosive properties.
5. Give military uses and reasons therefor.
6. Give method of determination of acidity.
7. Give precautions necessary for handling and storage.

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Chapter XIII.

1. Describe the preparation of mercury nitrate.
2. Give methods of combining the mercury nitrate and alcohol.
3. Describe the appearance of fulminate crystals.
4. What impurities must be avoided?
5. Describe briefly the stability and sensitiveness of fulminate.
6. Give reason for using potassium chlorate with fulminate.
7. What precautions are necessary in handling and storage?

Chapter XIV.

1. What is amatol?
2. Where and for what reasons was it adopted as a military explosive?
3. What mixtures are authorized?
4. What is the effect of impurities in T. N. T. used?
5. What impurities are to be avoided in the ammonium nitrate used?
6. Is amatol hygroscopic?
7. What effect has amatol on copper or tin?

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INTRODUCTION.

An *explosive* may be defined, in general, as being a liquid or a solid substance, or mixture of substances, which upon application of a blow to a small portion of its mass or by a rise in temperature, is converted in a small space of time into other substances more stable, which are mainly gases or vapors, but may include solids. The chemical changes thus produced develop a sudden rise in pressure in the surrounding medium, and the word "explosive" is applied as a general term to the different types of phenomena occurring in this sort of reactions. Coincident with this evolution of gas a considerable amount of heat is evolved which produces a flame. A *high explosive* is one in which this change occurs within the shortest space of time and the phenomenon accompanying this decomposition is termed a detonation. Detonation, therefore, applies, more properly, to the chemical reaction incident to the almost instantaneous decomposition of the high explosive; it is not properly employed, however, when discussing the analogous reaction incident to the combustion of a slower burning explosive as smokeless powder. The general term, *explosive*, which finds universal acceptance, applies alike to high explosives, black powder, and smokeless powder. It will be seen, therefore, that the accepted distinction between the different classes of explosives is based primarily upon their relative speed of decomposition, and only those explosives are classified as *high explosives* in which this chemical change is considered practically instantaneous.

Berthelot (Explosives and Their Power—Trans: Hake & Macnab—John Murray, London) enumerates and distinguishes between eight different groups of explosive bodies which owe their transformation either to the application of some external circumstance, such as fire, shock, friction, or else to the aid of a secondary reagent or chemical agent which propagates within itself an explosive wave and finally accomplishes a general explosion. Of these eight groups the greater number of military explosives fall within the third, fourth, and eighth divisions:

(*a*) *Explosive inorganic compounds.*—Definite bodies liquids or solids, as the azides.

(*b*) *Explosive organic compounds.*—Definite bodies, liquids or solids, in which classification occurs the nitrated derivatives of the carbohydrates, as nitrocellulose, nitrostarch, and the nitrated derivatives of the aromatic compounds as trinitrotoluene.

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(*c*) Mixtures formed by oxidizable and oxidizing bodies, solid or liquid, neither of these being explosives separately, as, for instance, black powder, etc.

Marshall (Explosives, Blakistons & Co., 1917, vol. 1) defines an explosion thus: "When gas or vapor is released so suddenly as to cause a loud noise an explosion is said to take place, as, for instance, the explosion of a steam boiler or of a cylinder of compressed gas." The barrel of the gun may be considered, at the time of the explosion, as being a cylinder of compressed gas. The walls of the gun constitute the walls of the cylinder, the breech mechanism one end, and the projectile the other.

If an explosive were used which gave instantaneous detonation the force so generated would either burst the barrel of the gun or else (in the case of a reduced charge) would not impart sufficient velocity to the projectile to develop the maximum efficiency. This particular point illustrates the necessity of using a relatively slow burning explosive as the means of propelling the projectile from the muzzle of the gun, an explosive which may be designated as the propelling charge or propellant. The compression in the powder chamber of the gun must be developed slowly at first, gradually increasing in intensity until the projectile, in the case of the ideal gun, is forced to the muzzle, at which place the maximum pressure of the charge is exerted. However, in actual practice the maximum compression in the gun is never developed at the muzzle, a condition which would cause bursting according to our present design, in which the maximum pressure is exerted just after the projectile starts moving from its original position; usually the maximum pressure occurs when the projectile is only 1 foot or so ahead of its original position. In this function of projecting a shot, the high explosive as such finds no application. It may occur, however, as a constituent of a propellant, as, for example, nitroglycerin, a high explosive which is an ingredient of certain sporting powders, pistol powders, and cordite powders. The field of usefulness of the high explosive as a class is quite different and advantage is taken of its properties of detonation to use it within the shell or other bursting projectile so that at the proper time the shell will be disrupted through the detonation of the high explosive with which it was filled.

The present tendency is to draw a sharp distinction between two classes of explosive bodies in accordance with the use to which they are put and also in accordance with the speed of reaction whereby combustion or decomposition takes place; for example:

First. Those substances or mixtures whose rate of combustion is such as to permit their use for propelling projectiles from guns are termed propellants.

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Second. Those substances whose rate of decomposition is so very high as to preclude their use as propellants, but which, on the other hand, bring about very powerful disruptive action. Such bodies are known as detonating explosives, disruptives, or more commonly, as *high explosive.*

The different substances used for high explosives are very many, but at the present time one substance, with certain modifications and additions, is used as the base of the propelling charge. This substance is a colloid formed by the action of a solvent upon a nitrated cellulose with or without the addition of nitroglycerin, and in its final form is called smokeless powder.

The selection of these various substances is dependent upon their cheapness of manufacture and their safety in handling. In order that this data may be properly evaluated, it is necessary that the following properties and measurements be determined:

First. The chemical equation involved in the change of the substance from the liquid or solid to the gaseous state.

Second. The thermo-chemical values as given in heats of formation of the different components.

Third. Their specific heats.

Fourth. Their densities.

Fifth. The relative pressure which may be developed by comparing equal parts of a new explosive with that of one well known.

Sixth. The type and amount of energy required to initiate reaction.

Seventh. Rapidity of reaction.

Eighth. The relative power of the explosive.

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CHAPTER I.

PART I.—PROPELLANTS.

MANUFACTURE OF SMOKELESS POWDER.

General.—The first nitro cotton which was made was the result of an experiment performed in 1838, when Pélouze observed the action of nitric acid upon cotton. A few years later, in 1845, Schonbein realized the importance of this material as an explosive and developed it to such a point that he endeavored to sell the product to various governments. Early attempts at the use of this new explosive, however, especially in Austro-Hungary, were fraught with disaster, for factories were destroyed, and guns were damaged as a result of unfamiliarity with the chemical and physical properties of this new substance.

The unfortunate experiences, however, of the Austrians did not deter the English chemists from developing the industry. Prominent among these men at this time was Sir Frederick Abel, who started a small factory for the manufacture of nitro cotton at Waltham Abbey. The industry received tremendous support and the important progress which was made during the next few years was, in fact, responsible for the later developments of collodion-photography and for the artificial silk industry.

During this period the use of gun cotton as an explosive was restricted entirely to blasting purposes. In seeking for a new material which might be used in place of black powder, and which would not have the objectionable features of the old propellant, as smoke, etc., it occurred to Schultze that gun cotton would be a possible substitute for this purpose. Many different substances and compounds were experimented with, but the first ones to achieve any notable success were the Schultze and the E. C. powders. These won instant recognition as shotgun powders, but proved too quick for use in rifled arms.

About this time another important step in the development of *smokeless powder* was made by Vielle, a French chemist. He incorporated nitro cotton with a mixture of ether-alcohol, and rolled the resulting paste, a colloid, into thin sheets, which were cut into small squares and dried. Contemporaneous with this work, Nobel developed ballistite, a powder obtained by gelatinizing a low nitrated nitro cotton with nitroglycerin. Shortly after this, a modification of ballistite, known as cordite, was adopted as a *smokeless powder.*

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This propellant consisted of a mixture of high nitrated gun cotton gelatinized by means of acetone. In this mixture nitroglycerin and vaseline were incorporated.

At the present time all nations use as a propellant either gelatinized nitro cotton alone, or else gelatinized nitro cotton mixed with varying quantities of nitroglycerin.

The term *smokeless powder* when considered from the exact meaning of the words is a paradoxical misnomer, for the substance is not entirely smokeless, and it is not a powder.

It may occur in small flakes, strips, pellets, cylinders, or other different shapes, the cylinders varying in length from 1.45 millimeters for 8 mm. gun to 55 millimeters for a 16-inch gun. The accepted form of granulation of *smokeless powder* used in this country is that of a cylinder in which extend longitudinally one or more perforations throughout the grain. For the smaller size powders, as for instance 8 mm., .30 caliber, 1 pounder, etc., there is only a single perforation. The larger sizes, however, have seven perforations. There is no intermediate number of perforations, the grain either having one or else seven.

In addition to the cylindrical form of granulation, the so-called Walsh grain, or sliverless grain, has been devised to meet certain conditions incident to the firing of mortars. Instead of being a true cylinder the grain is scalloped on the outer surface. There are six of these indentations, and they are so placed that the apex of the reentrant angle occurs exactly at a point midway between the six outside perforations. This form of grain accomplishes the important function that it reduces the weight of the charge, for the reason that its combustion is practically complete. This is due to the fact that the burning surface is greater than that of the cylindrical grain of the same length and the same diameter. This greater burning surface gives an increased rate of burning, with the result that where formerly there was a relatively large amount of unconsumed powder left after the charge had been fired with the use of this type of grain the slivers of unburned powder are practically eliminated. It dries also quite as well, if not better, than the cylindrical grain and shows no tendency to split at the reentrant angles.

MANUFACTURE.

The different processes incident to the manufacture of *smokeless powder* may be summarized under the following heads:

First. Purification and mechanical preparation of the raw cotton. This includes the picking and drying processes.

Second. Nitration of the cotton. This is accomplished by treating the cotton with a mixture of nitric and sulphuric acids, thus producing a cellulose nitrate or "pyro cotton."

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Third. The purification of the "pyro" from all traces of free acids and lower nitrates.

Fourth. The mixing of the pyro cotton with ether-alcohol to form a colloid.

Fifth. The granulation of the powder by pressing the colloid through steel dies.

Sixth. The final processes of solvent recovery, drying, and blending.

The details of manufacture are as follows:

The cotton used in the manufacture of *smokeless powder* consists in the main of two distinct grades: The one known as linters and the other as hull fiber. Depending upon the availability of these different grades, various mixtures of the two are generally used. The object of the bleaching is to reduce the extractive matter to less than 0.4 per cent, and the ash to 0.8 per cent. The presence of chlorides, sulphates and lime in amounts larger than traces is likewise objectionable. If, on the other hand, the cotton is overbleached, a relatively large amount of cellulose soluble in 10 per cent KoH solution is formed. This material, called "soluble cellulose," is objectionable from the standpoints of nitration, stability, and yield, and the amount present in the bleached cotton should not exceed 7 per cent. In other words, overbleaching is to be avoided. If uniform nitration is to be obtained it is essential that the cotton must be of uniform moisture content, of a uniform physical condition, and that it should be free from lumps or any extraneous material.

(*a*) *Picking of cotton.*—To obtain this uniformity the cotton is put through a picking machine of which there are various forms, e. g., the Cogswell Mill, the Cyclone Superior, and the Davis & Furber picker. The last-mentioned machine is provided with a toothed roller which engages the cotton as it is moved along the feeding table, and carries it into such a position that it is caught and torn apart by rows of sharp hook-shaped teeth set along six evenly spaced elements of a skeleton cylinder revolving at the rate of 1,050 revolutions per minute. This operation reduces the cotton to a fluffy state in which it is caught and blown by air blast into a large flue leading into the drying room.

(*b*) *Drying of cotton.*—Two systems of drying are in use: One the continuous dryer in which the cotton is conveyed by a belt through a long chamber heated to about 100° C., the other by placing the cotton in a large chamber which is heated by hot-air blast. The former is a continuous operation and the cotton issuing from the dryer is weighed directly into metal containers and transferred to the nitrating house. The entering cotton usually contains about 8 per cent moisture. The treatment reduces this to approximately 0.5 per cent.

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The chamber system is the more expensive of the two and the least desirable from the standpoint of time. These chambers are of such a size as to hold approximately 57 bales of cotton or 4,000 pounds. After the chamber has been filled, it is closed tightly and the heat is gradually raised until the temperature reaches 105° C., where it is held for 24 hours. After a laboratory test of the cotton has shown a satisfactory content of moisture, the dried cotton is weighed and sent to the nitrating house.

(*c*) *Nitrating.*—In the nitration of cellulose there are two reactions to be considered from the manufacturing standpoint. Although these reactions occur simultaneously, for the sake of clearness in description they are to be considered separately—first, the formation of the nitric acid-ester of cellulose, and the subsequent removal of the water formed in the reaction by sulphuric acid.

There are three kinds of acid used in nitrating, namely, fortifying, fuming sulphuric, and strong-spent acid. The strong-spent acid is that which is recovered from the nitrators after nitration has been completed. This acid is built up or fortified by use of a fortifying acid, having a strength of approximately 52.35 per cent nitric and 44.87 per cent sulphuric. This acid supplies all of the nitric acid necessary for the new nitration and a portion of the sulphuric acid. The rest of the sulphuric acid is supplied by adding fuming acid of 104 per cent H_2SO_4. The main function of the sulphuric acid is to combine with the water formed during the reaction, and in this manner to prevent the dilution of the nitric acid. In addition to this, however, it evidently plays an important part in the actual nitration by first converting a part of the substance, in this case cellulose, either into a sulphuric ester or to a sulphonic acid, which in turn is more readily acted upon by the nitric acid. The mixing of these acids of different specific gravities has been a subject of a good deal of argument on the part of the several large manufacturing companies concerned. At the present time this mixing is generally accomplished by iron paddles rather than by the use of compressed air.

Four different systems of nitration have been used in this country, viz: The Du Pont mechanical dipper process, the centrifugal process, the Thompson displacement system, and the pot process. The relative proportions of the nitric acid, sulphuric acid, and water vary not only with the different processes, but also with a change in weather conditions, more particularly of temperature. The sulphuric acid content is maintained very nearly constant, but the variation in nitric acid is nearly 1 per cent, and is largely accounted for by the fact that a certain amount of denitration of nitro cotton takes place during warm weather. Unless the nitric is increased to take care of this phenomenon, the resulting nitro cotton will be below specifications.

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1. *Du Pont mechanical dipper process.*—The entire cycle of operation in this process is not more than 35 minutes. Under ordinary working conditions the fumes are negligible, whereas in all of the other nitrating systems the fumes are always in evidence, so that from the standpoint of the health of the operatives the Du Pont system is much to be preferred, provided that the proper care is always exercised in the manipulation of the machinery.

A nitrating unit in this system consists of four iron pots so situated that they can all be handled from a center point. In each nitrator there are two vertical revolving paddles operated in opposite directions from each other, the motion being from without inward. These paddles consist of a series of horizontal arms so placed upon the post that when set in motion the cotton is quickly drawn beneath the surface of the acid. A charge of approximately 1,440 pounds of acid per nitrator is used, of which the following is a fair average composition: HNO_3, 20.71 per cent; H_2SO_4, 62.83 per cent; N_2O_4, 0.79 per cent; H_2O, 15.67 per cent.

When the acid has been run in the paddles are set in motion and 32 pounds of cotton added. The speed of these paddles varies according to the stage of nitration. At first during the period when the cotton is being immersed in the acid the speed is 72 revolutions per minute. During the time of nitration, which is usually from 18 to 24 minutes, the speed is cut to 36 revolutions per minute. Finally, when the nitrator is about to be discharged the agitation is again as violent as possible, and the speed is raised to that maintained during the immersion process. The bottom discharge pipe is then opened and the cotton and acid are let down into a centrifugal wringer.

2. *Centrifugal process.*—In this system the nitrating and the separation of the spent acid from the nitrated cotton are both carried on in a large nitrating centrifugal. The latter is filled with a definite amount of the mixed acid, usually 50 times the weight of the cotton charge, at a temperature of about 32° C., the weighed charge of cotton (usually 30 pounds) immersed rapidly by means of an iron fork and allowed to stand for about 20 minutes, with occasional turning over by means of the fork. The drain cock is then opened and the spent acid separated by centrifuging, after which the charge is forked out and drowned, as in the mechanical dipper process.

3. *Pot process.*—In the pot process the nitration is best carried out in iron pots. These are filled with the mixed acid, the cotton immersed and allowed to digest for 20 to 30 minutes, when the entire contents are dumped into a centrifugal wringer. The pots are moved and dumped by means of a suitable two-wheeled truck conveyer. The pot process employs considerably less acid than the centrifugal process, about 35 parts of acid being sufficient to properly cover the

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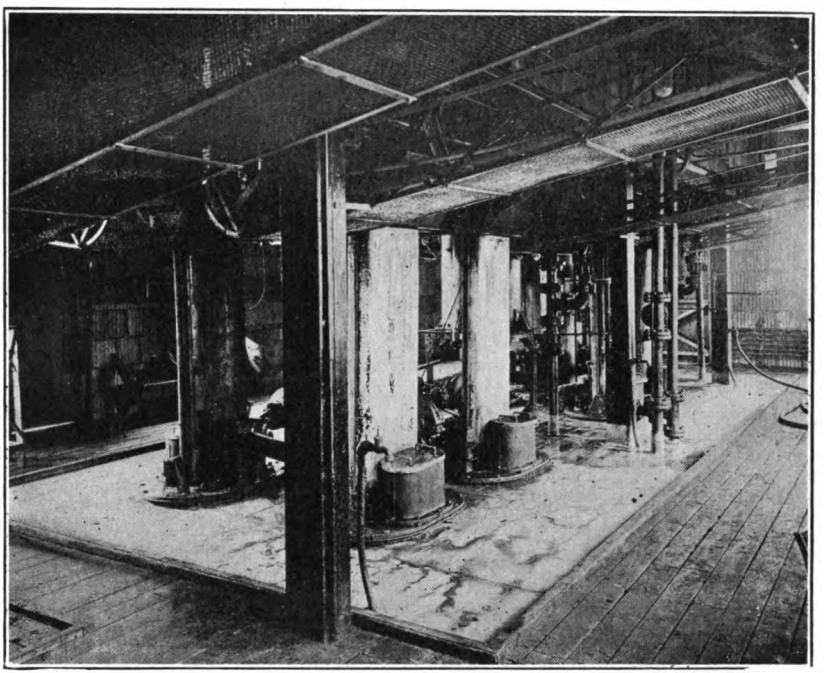

PLATE 1.—DU PONT MECHANICAL DIPPER PROCESS, NITRATING FLOOR, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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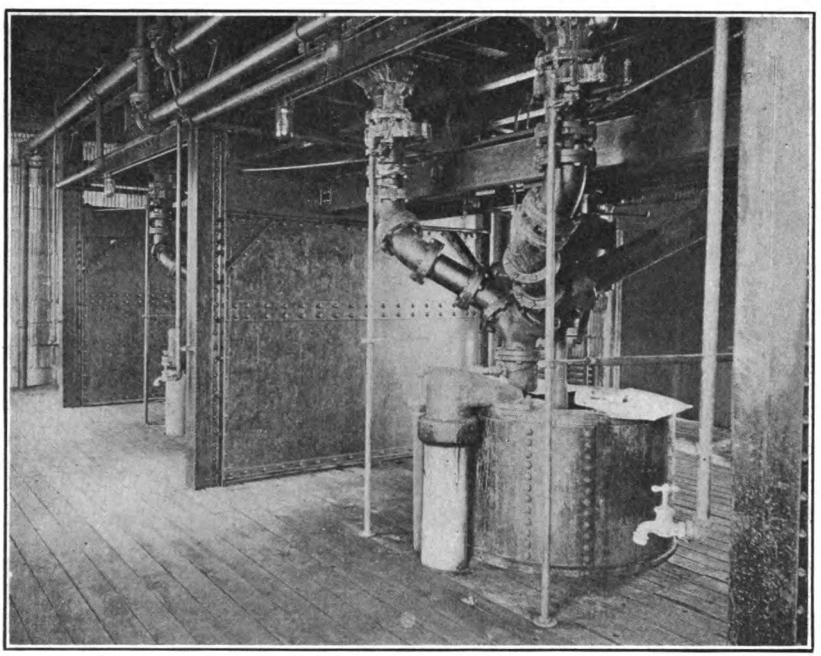

PLATE 2.—DU PONT MECHANICAL DIPPER PROCESS, WRINGING CENTRIFUGAL FLOOR, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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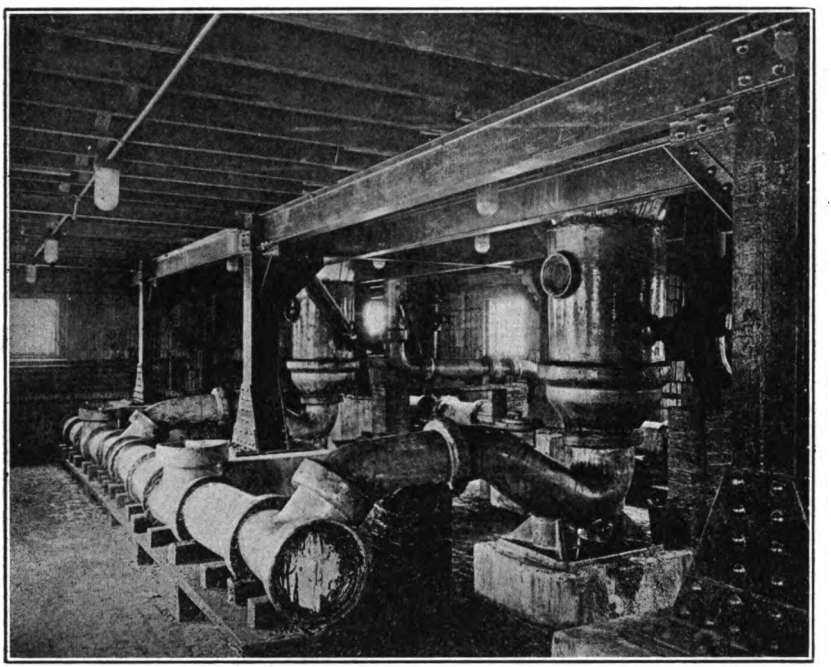

PLATE 3.—DU PONT MECHANICAL DIPPER PROCESS, IMMERSING BASIN AND EXIT FLUME FLOOR, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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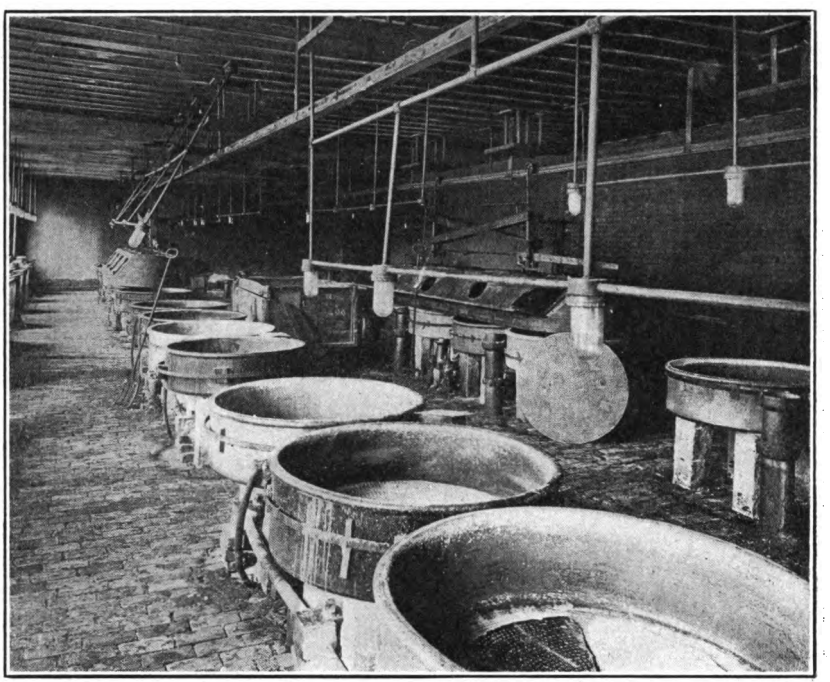

PLATE 4.—NITRATING PANS, THOMPSON DISPLACEMENT PROCESS, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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cotton. The charge of cotton used is generally about four pounds. Sometimes much smaller pots made of earthenware are used, holding a charge of only 2 pounds of cotton, several of these charges constituting a wringer charge. These small pots are usually emptied by hand.

4. *Thompson displacement system.*—This process has been employed in this country only at Picatinny Arsenal and at present has been discarded in favor of the mechanical dipper process. The nitration takes place in shallow pans, about 4 feet diameter and 14 inches deep, made of heavy earthenware. The cotton (22½ pounds) is immersed in 800 pounds of mixed acid at 30° C., mixed thoroughly with a fork, and allowed to digest for 1 hour. The charge is then

SCHEMATIC SKETCH OF UNIT OF NITRATING HOUSE.

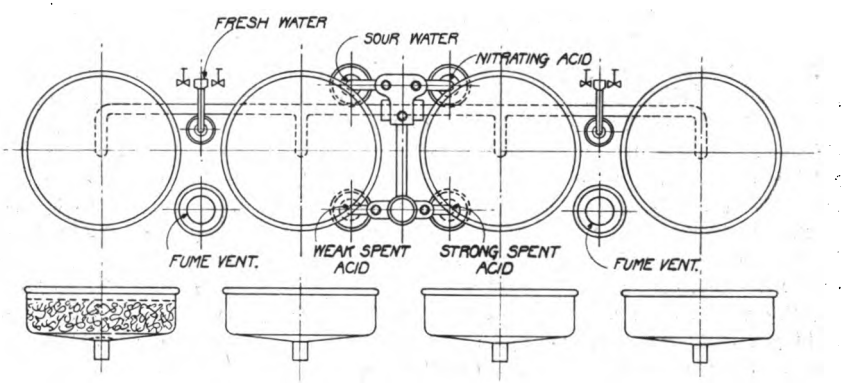

PLATE 5.

covered with a perforated porcelain plate on top of which cold water is allowed to run slowly while the spent acid is drawn off at an equal rate from the bottom of the pan. There is thus only a slight mixing of the water with the upper layers of acid. The spent acid drawn off in the first 45 minutes is of sufficient strength to be fortified for further use; that drawn off in the next 10 minutes is "weak spent acid," which is sent to the denitrating and concentrating plant for recovery, while the remainder, called "sour water," goes to waste. The chief disadvantage of the process is that the slight dilution of the spent acid in the zone of contact with the water causes an appreciable denitration of the nitro cotton, resulting in nonuniformity of the nitrated charge. It is also slower in point of time consumed, but on the other hand is more safe from the standpoint of fires. The charge, when removed from the pan, is ready for the boiling treatment.

The object here is to throw the free acid through the basket in the shortest possible space of time. Most of the fires which occur in the

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process are the so-called "wringer fires," and are the result of the operatives failing to follow instructions relative to speed of wringer and method of discharge. The cotton is wrung for five minutes and then discharged into an immersion basin below. As fast as the cotton falls into the basin it is submerged by a heavy stream of water distributed by a fishtail or some other form which combines the greatest dispersion of water with the maximum force for submerging. Following this the pyro, as it is now called, is transferred by means of pumps or by gravity to the boiling tub house.

The spent acid recovered from the centrifugals is transferred to storage tanks to be fortified, as has already been mentioned. Its average composition is approximately: HNO_3, 17.96 per cent; H_2SO_4, 64.60 per cent; N_2O_4, 0.67 per cent; H_2O, 16.77 per cent.

The chemical reactions involved in the nitration are not understood definitely, for the reason that the exact molecular weight of cellulose is not known. The empirical formula of cellulose is assumed to be $(C_6H_{10}O_5)_x$, and is thus discussed by Marshall (Explosives, Arthur Marshall, Blakiston's, 1917, pp. 135–136):

At first the simplest possible formula was assumed for cellulose, $C_6H_{10}O_5$, and guncotton of high nitrogen content and low solubility in ether-alcohol was supposed to be formed by the substitution of three NO_2 groups for hydrogen atoms, $C_6H_7O_5(NO_3)_3$, and was consequently called trinitro-cellulose. The less nitrated product soluble in ether-alcohol was similarly supposed to be the dinitro-cellulose $C_6H_8O_5(NO_2)_2$. Later workers obtaining evidence of intermediate stages of nitration proposed to increase the formula of cellulose; Eder doubled it, Vielle quadrupled it, and Mendeleeff octupled it, giving 48 atoms of carbon to each molecule, and hydrogen and oxygen in proportion. A nitro-cellulose having the composition of the above-mentioned trinitro-compound would contain 14.14 per cent nitrogen. Quite as much as this has never been found by the analysis of any product that has ever been obtained, but various investigators by nitrating with mixtures of nitric acid and phosphorus pentoxide, or with concentrated sulphuric and nitric acids and extracting the product with ether-alcohol have obtained percentages between 13.9 and 14.4. Lunge and Bebie found that with mixtures of sulphuric and nitric acids the highest percentage of nitrogen was attained, not with anhydrous acids, but with mixed acids containing 11 or 12 per cent of water: with a mixture in which the proportions $H_2SO_4:HNO_3:H_2O$: were 63.35 : 25.31 : 11.34 they produced a nitro cotton containing 13.92 per cent N, but this was not stable. After keeping in the wet state it was reanalyzed and found to contain then only 13.5 per cent N, and other nitro cottons nitrated almost as highly were found to decompose rapidly until the same composition was reached, even though the material was kept under water. This corresponds very closely with the formula $C_{24}H_{29}O_{20}(NO_3)11$, endeka-nitro-cellulose. Hence the authors conclude that the molecule with 24 atoms of carbon fits the facts sufficiently well, but point out that this is only the lower limit of the possible size of the cellulose molecule, as to the real magnitude of which there is little or no evidence.

With the possible exception of this endeka-nitro-cellulose no definite stages of nitration can be recognized; nitro-celluloses with every percentage of nitrogen from 7 to 13.5 and more can be produced, and those of the same degree of

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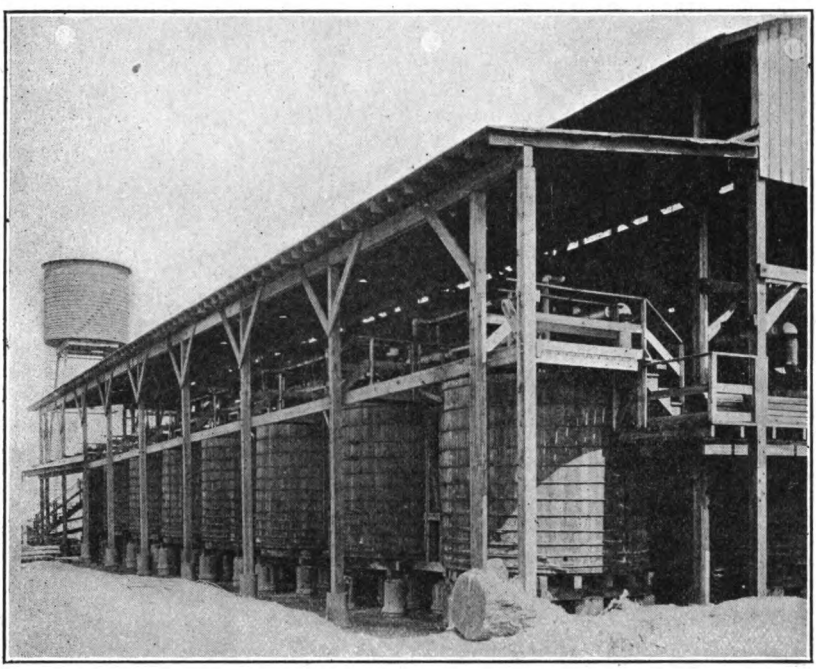

PLATE 6.—EXTERIOR OF BOILING TUB UNIT, OLD HICKORY SMOKELESS POWDER PLANT, NASHVILLE, TENN.

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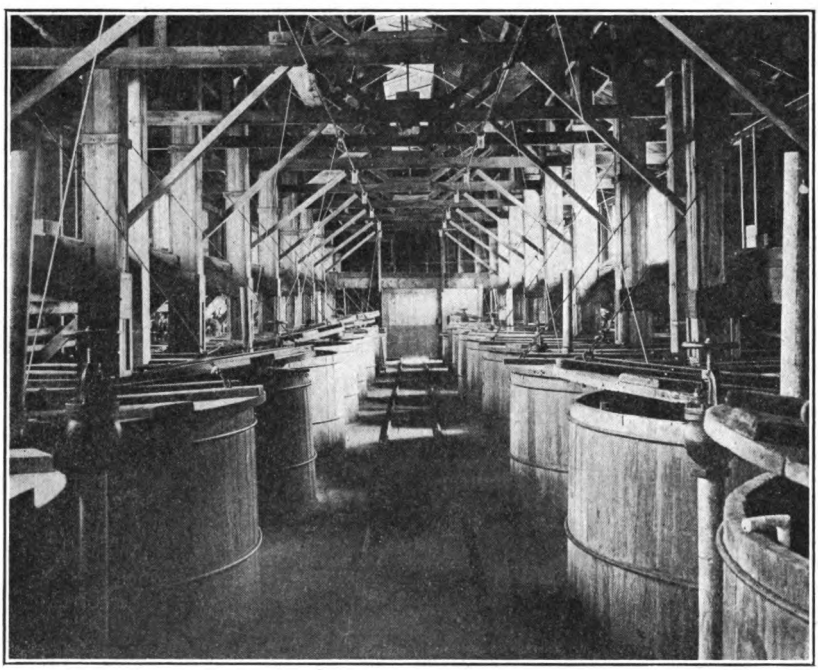

PLATE 7.—INTERIOR OF BOILING TUB UNIT, OLD HICKORY SMOKELESS POWDER PLANT, NASHVILLE, TENN.

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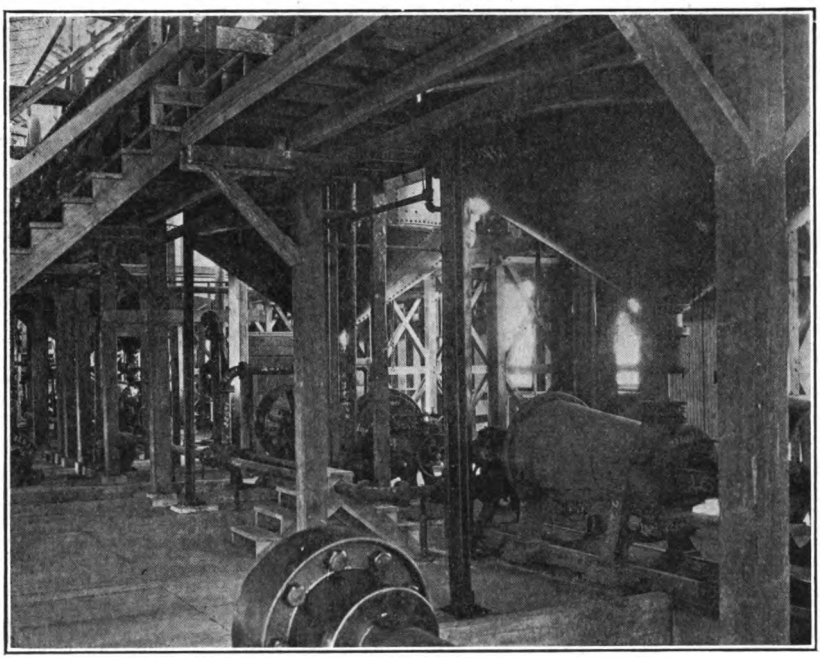

PLATE 8.—JORDAN PULPING ENGINE UNIT, OLD HICKORY SMOKELESS POWDER PLANT, NASHVILLE, TENN.

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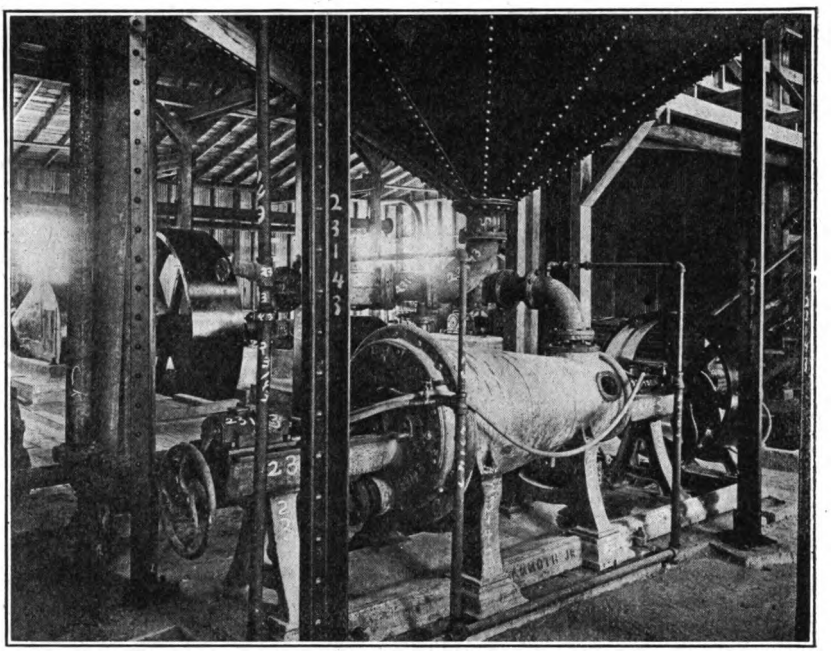

PLATE 9.—JORDAN PULPING ENGINE UNIT, OLD HICKORY SMOKELESS POWDER PLANT, NASHVILLE, TENN.

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nitration may be soluble to very different extents in ether-alcohol. To characterize a nitro cotton it is better to specify the percentage of nitrogen and the solubility rather than to state the number of NO_2 groups that it is supposed to contain in each molecule. The following table shows the percentage of nitrogen and the volume of gas evolved in the nitrometer by the different nitro-celluloses of the C_{24} series. The figures have been calculated, using the latest atomic weights.

Designation.	Formula.	c.c. NO per lg.	Per cent N.
Dodeka-nitro-cellulose	$C_{24}H_{28}O_{20}(NO_2)12$	225.6	14.14
Endeka-nitro-cellulose	$C_{24}H_{29}O_{20}(NO_2)11$	215.0	13.48
Deka-nitro-cellulose	$C_{24}H_{30}O_{20}(NO_2)10$	203.5	12.76
Ennea-nitro-cellulose	$C_{24}H_{31}O_{20}(NO_2)9$	190.9	11.97
Okto-nitro-cellulose	$C_{24}H_{32}O_{20}(NO_2)8$	177.3	11.12
Hepto-nitro-cellulose	$C_{24}H_{33}O_{20}(NO_2)7$	162.4	10.18
Hexa-nitro-cellulose	$C_{24}H_{34}O_{20}(NO_2)6$	146.0	9.15
Penta-nitro-cellulose	$C_{24}H_{35}O_{20}(NO_2)5$	127.9	8.02
Tetra-nitro-cellulose	$C_{24}H_{36}O_{20}(NO_2)4$	107.9	6.77

Escales (Die Explosivstoffe mit besondere berucksichtignung der Neuren Patente, Bearbitet von, Dr. Richard Escales, Leipzig, von Veit, 1914) discusses the cellulose nitrate from a slightly different standpoint, as shown by the appended table.

Composition of cellulose (nitrated).

Parts nitrate.	Designation.	Formula.	c.c. NO per lg.	Per cent N.
12	Dodeka-nitro-cellulose	$C_{24}H_{28}O_8(NO_2)12$	226.27	14.14
11	Endeka-nitro-cellulose	$C_{24}H_{29}O_9(NO_2)11$	215.17	13.47
10	Deka-nitro-cellulose	$C_{24}H_{30}O_{10}(NO_2)10$	203.35	12.75
9	Ennea-nitro-cellulose	$C_{24}H_{31}O_{11}(NO_2)9$	190.75	11.96
8	Okto-nitro-cellulose	$C_{24}H_{32}O_{12}(NO_2)8$	177.19	11.11
7	Hepto-nitro-cellulose	$C_{24}H_{33}O_{13}(NO_2)7$	162.36	10.18
6	Hexa-nitro-cellulose	$C_{24}H_{34}O_{14}(NO_2)6$	145.96	9.15
5	Penta-nitro-cellulose	$C_{24}H_{35}O_{15}(NO_2)5$	127.91	8.02
4	Tetra-nitro-cellulose	$C_{24}H_{36}O_{16}(NO_2)4$	107.81	6.76

It should be definitely understood that nitrocellulose is not a true nitro body, but is a nitric-acid-ester, or nitrate of cellulose. Nitrates yield all their nitrogen as nitric oxide (NO) in the nitrometer; nitro bodies do not. Hence the term "nitrocellulose" is also a misnomer, but has become standard through long usage. The same remarks apply to nitroglycerin and nitrostarch.

In the nitration of the cotton there are two things to be accomplished: First, the formation of a product containing a high percentage of nitrogen; and second, the formation of a product which will be 99 per cent soluble in a mixture of two parts ether and one part alcohol. A correctly prepared pyro should contain 12.60 per cent $N \pm 0.1$ per cent, and corresponds very closely to the deka-nitrocellulose. The solubility phase is very important for the reason that the nitro cotton is eventually converted into a dense

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colloid, the properties of which depend upon the solubility of the nitrocellulose. If this colloid is of low solubility the resulting granulation will lack in uniform consistency, due to the fact that there will be white particles of uncolloided cotton throughout the mass.

(*d*) *Purification.*—Under the general term of purification is included the following sequence of processes: Preliminary boiling, pulping, poaching, screening, and wringing. It is impossible with our present limited knowledge of the cellulose molecule and of the intermediate reactions occurring during the nitration of the molecule, to control the reaction to such an extent that a nitrocellulose, consisting of but one nitro body, will result from a certain reaction accomplished under a set of standard conditions. The products of the reaction always include certain of the lower nitrocelluloses. These bodies influence the stability of the whole mass and must, therefore, be removed before the stability of the pyro cotton can be guaranteed. The object then of the purification treatment given to the pyro is to insure a uniform stability by eliminating, through hydrolysis or other means, these unstable lower nitro bodies. This is accomplished most easily by prolonged boiling in water, which in the preliminary treatment has an acidity varying from 0.1 to 0.3 per cent calculated at H_2SO_4.

The preliminary boiling process is carried out in large wooden tubs, constructed preferably of cypress and having a false bottom. Underneath this false bottom is a system of steam pipes which provide the means of bringing the contents of the tub to the boiling point. The tubs hold about 1,200 pounds of pyro cotton. After charging a tub with cotton cold water is run in until the cotton is entirely submerged. The steam is then turned on and the contents of the tub boiled for 16 hours. During this process it is necessary to add additional water from time to time so that none of the cotton becomes exposed to air. The actual boiling time must be 16 hours. The steam is then turned off, the tub refilled and boiled again for 8 hours. This is repeated until each tub has had a 40-hour boil, with not less than four changes of water. Careful attention to the details in the boiling-tub house insure to the finished pyro cotton a higher ether-alcohol solubility and a more satisfactory stability than one in which these details have been disregarded.

Pulping.—The next process, that of pulping, has for its object the reduction of the cotton fibers to a uniform state of division so that subsequent formation of a colloid by means of the ether and alcohol mixture will be entirely uniform. The degree of fineness is determined by laboratory test and has been the subject of a great deal of discussion. It has been maintained by some manufacturers that a finely cut pyro produces a powder inferior in toughness to that made from a

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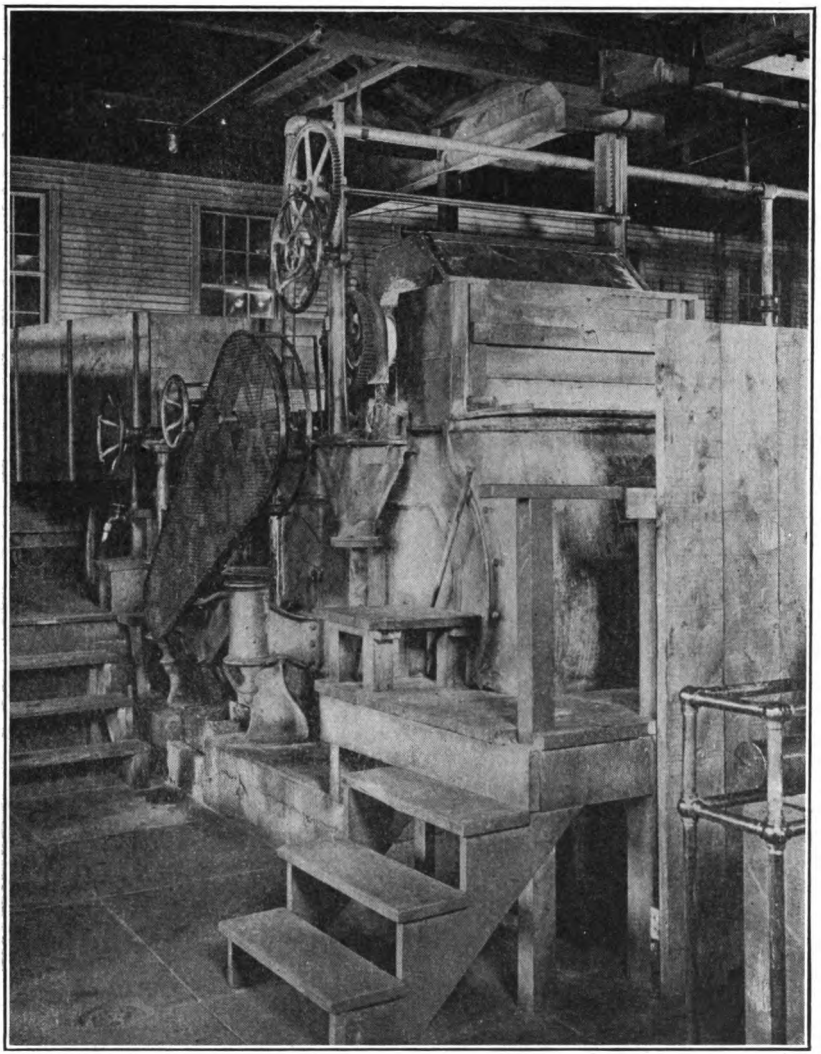

PLATE 10.—MILLER-DUPLEX TYPE BEATER, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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PLATE 11.—INTERIOR OF POACHING HOUSE, OLD HICKORY SMOKELESS POWDER PLANT, NASHVILLE, TENN.

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coarser cut pyro, but since the colloiding operation tends to destroy the fibrous condition of the cotton, it does not appear to be altogether reasonable to assume that the degree of fineness of pyro has an appreciable effect upon the toughness of the finished powder. The pulping operation is accomplished by machines similar to those used in the paper industry.

The most efficient means for pulping cotton is provided by the Jordan machine. This is operated on the centrifugal principle, by means of which the entering cotton is thrown from the large end of the beater to the small tapered end, and from thence to a storage tank over the machine. The more efficient way of running these units is to have them adjusted in such a manner that the cotton is given a progressive cut. In other words, the first Jordan machine will give only a fairly coarse cut to the cotton, the next a little finer, and so on, until the cotton has finally been pulped to the necessary degree of fineness.

The other types of machines used for this purpose are either the Jordan beater or the Miller duplex beater. The essential features of a pulping machine consist of a fixed set of knives at the bottom of a tub over which revolves a roller which is mounted in adjustable bearings and carries a removable set of knives. The pulping is accomplished by the rolls repeatedly drawing the pyro cotton between the two sets of knives and thus reducing the material to any desired degree of fineness. A weak soda solution is used during this process for the purpose of neutralizing the acid retained within the fibers of the cotton and which is set free mechanically when these fibers are macerated.

With the Miller duplex beater the hull fiber is cut in a much shorter time than the linters, the variation being between six and eight hours per beater lot. During the first stage of the pulping treatment, a washer, consisting of a large octagonal box covered with very fine wire screen, is lowered into the pulp to remove a part of the sour water, fresh water being added at the same time. The water thus removed passes to settling basins where any pyro carried off mechanically is recovered. When the desired degree of fineness has been obtained, the material is ready for the next purifying process.

Poaching.—It has already been pointed out that in the pulping operation the fibers of the cotton are broken down mechanically so that the original physical texture of the cotton is destroyed. The preliminary boiling tub treatment reduced the acidity of the fibers and of the interstitial material, but the pulping process, by macerating these fibers, has set free an additional amount of acid. It is, therefore, necessary to repurify the cotton by boiling. This opera-

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tion is carried on in the poacher house in a manner somewhat similar to that described in the boiling tub house, but with the notable difference that the first boiling treatment is carried out in an alkaline solution. For this purpose there is dissolved 1 pound of sodium carbonate (soda ash) to a gallon of water, and for every 2,000 pounds of dry nitrocellulose there may be added 10 gallons of this solution. It is necessary to repeat the boiling operation five times, but the soda is only added during the first boiling. All the other treatments are made in a neutral solution. During all of these treatments a thorough agitation of the cotton is essential so that it is necessary to employ mechanical stirrers driven by gears and shafting. At this stage of the operation it is necessary for the chemical laboratory to determine: (*a*) The stability of the cotton by K. I. test and 135° test, (*b*) the percentage of nitrogen in the cotton, (*c*) the solubility of the cotton in the ether-alcohol mixture, (*d*) the degree of fineness, and (*e*) the ash. The details of performing these analyses are described in another chapter.

After purifying the pyro-cotton, as described above, it is necessary to separate mechanically any foreign material or any portions of the cotton which may not have been properly macerated in the beater house. This is accomplished by means of the Packer pulping screen. This piece of machinery consists of a large box, the bottom of which is fitted with a brass plate having slits one one-hundreth inch in width. The cotton is drawn through these slits by suction underneath the screen and any particles which are too coarse to pass through are returned to the beater house for additional treatment. From the Packer screen the cotton is pumped into one of the large blending tubs where it is stored until needed in the next operation.

Wringing.—The transference of the cotton from the time of nitration up to this stage of manufacture is accomplished by having the cotton suspended in water. It is the function of the wringers to remove all of the excess water from the cotton so that the subsequent operation of dehydrating by means of alcohol will be done with the minimum amount of water present. This wringing operation consists merely in forcing the water out of the cotton by means of centrifugal action.

The wringer consists of a wire basket of such a mesh that the cotton is held within the screen. This basket is connected by means of a shaft to a motor, and is so geared that the basket revolves at a speed of 800 revolutions per minute. This centrifugal action forces the water out of the cotton through the basket and so on down the drain pipe. At the end of this operation another sample is sent to the laboratory for the purpose of determining the amount of moisture

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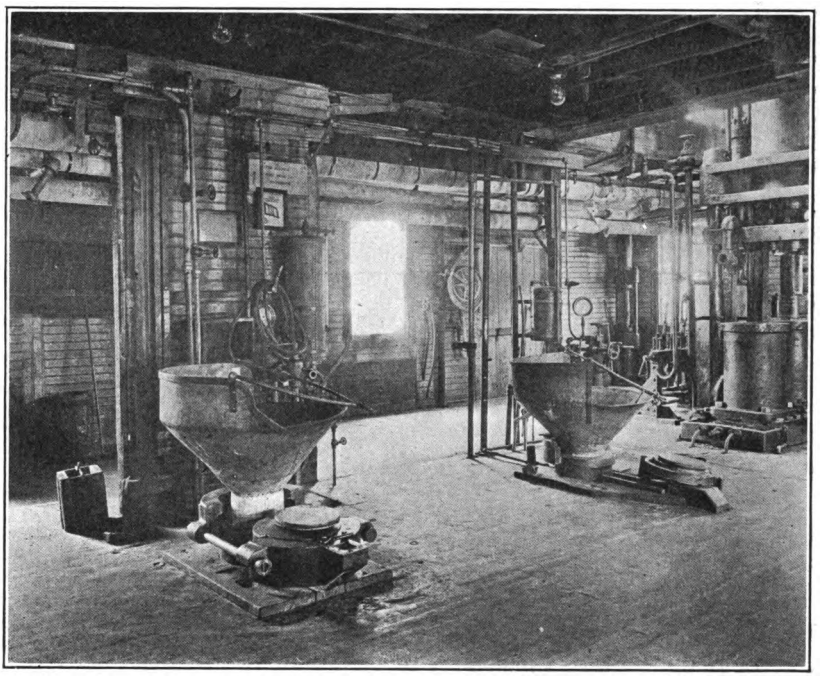

PLATE 13.—OPERATING FLOOR, DEHYDRATING PRESS HOUSE, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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remaining in the cotton. This should average between 28 and 30 per cent. It is necessary to maintain the moisture at this figure in order to insure safety from the standpoint of fire.

If the wringers are operated at a uniform rate of speed for the same length of time the moisture content will not vary more than 2 per cent. This operation concludes the manufacture of pyro cotton

SCHEMATIC SKETCH OF PACKER PULP SCREEN.

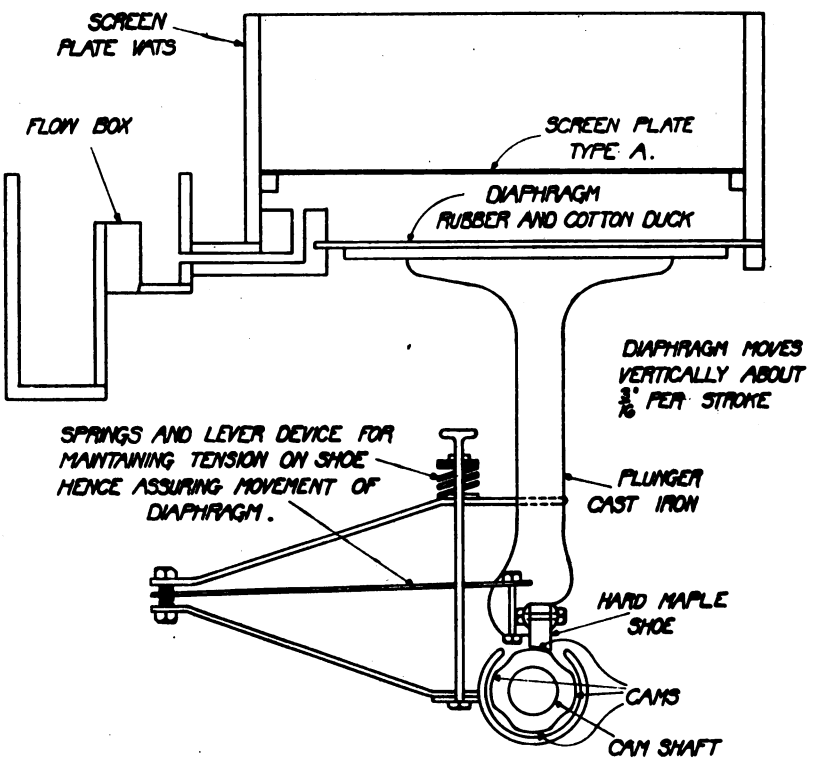

PLATE 12.

and the material from this time on loses its identity as such and is called, for the want of a better word, the "colloid" or the "powder."

Dehydration.—The pyro from the wringers, containing approximately 30 per cent moisture, is transferred to storage and placed in warehouses to prevent freezing in winter time until it is required for dehydration. The object of this operation is to remove all of the water from the pyro and to add in its place the quantity of alcohol necessary to form the colloid. This amount varies within relatively small limits and is dependent upon the solubility of the pyro being used, as shown by laboratory tests, and also, to a certain extent, upon the

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size of granulation of the final powder. It is customary to add 1¼ pounds of alcohol for every pound, dry weight, of cotton.

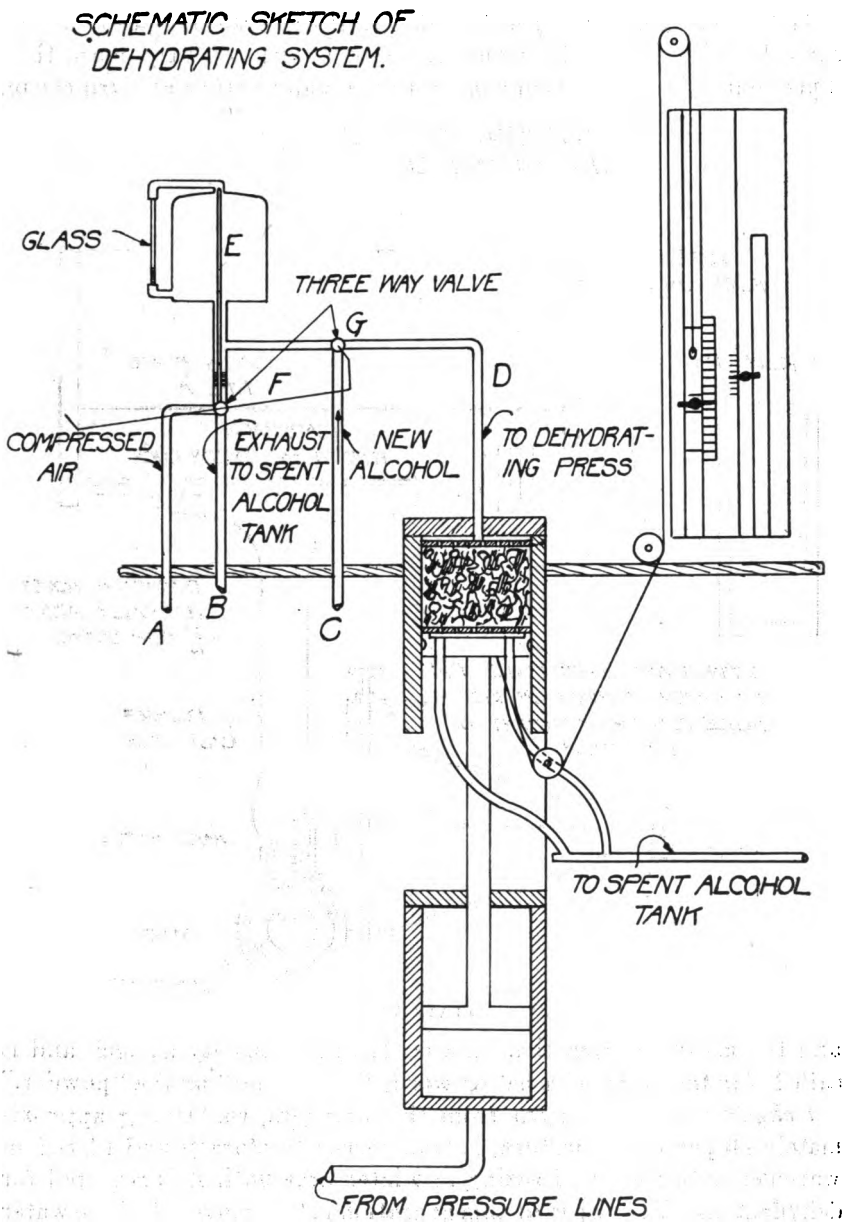

PLATE 14.

The amount of solvent (ether-alcohol) necessary to form the colloid is determined from previous experience of manufacture and is correlated with ballistic data obtained from the proving ground. For certain types of gun it has been found that 100 per cent solvent (67

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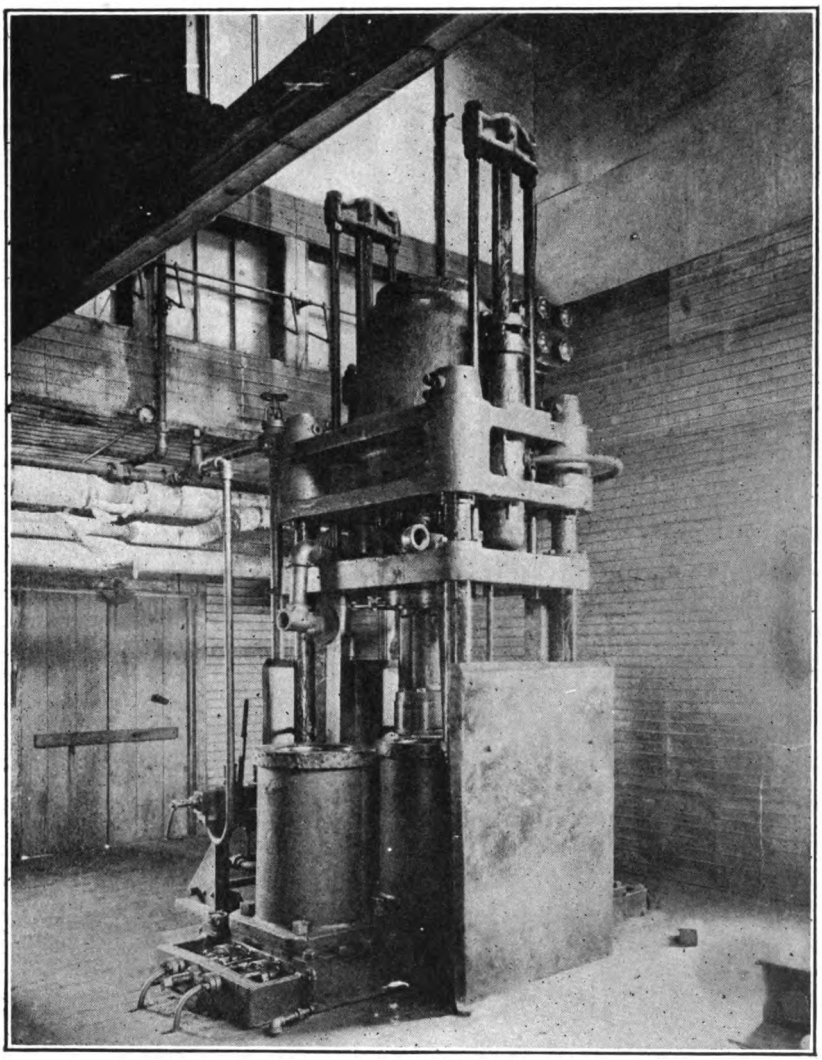

PLATE 15.—LARGE DEHYDRATING PRESS, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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per cent ether and 33 per cent alcohol) produces a colloid which will give the most uniform results from the standpoint of graining and also from the standpoint of firing. In the event that 100 per cent solvent is to be used or 1 pound of solvent for every pound of pyro, it will be necessary that the original block of 25 pounds dry weight of pyro be increased to 33 pounds 4 ounces.

The dehydrating operation is conducted somewhat as follows: The press consists of a cylinder and movable piston operated by hydraulic pressure, as indicated on the attached sketch. The press is charged with pyro and "low pressure" (about 1,200 pounds per square inch) is applied for a few moments, thus squeezing out a portion of the excess water in the cotton. The predetermined amount of alcohol is then forced into the press by use of a pump, and the pressure then increased to about 3,700 pounds per square inch. The alcohol functions first as a displacing agent and finally as a dehydrating agent. Its initial entrance into the block forces out a small portion of the remaining water; later, however, it combines with the residual water and produces a block of pyro nearly free of water. The first portion of this alcohol contains relatively large amounts of water and is forced out of the press into the spent alcohol tank. The remaining amount, however, is nearly 90 per cent alcohol. The spent alcohol resulting from this process is pumped back into the storage tank and eventually sent to the ether still for the manufacture of pure ether.

The subject of changing the point of exit of the spent alcohol from the bottom of the block to the top of the block has been discussed by some of the manufacturing companies and is in fact in operation by certain plants. This change in method is technically known as the "full back up" system of dehydrating as differentiated from the "no back up" system. Proponents of this new system claim that the residual alcohol remaining in the dehydrated block contains a smaller percentage of water than alcohol remaining in a block which was dehydrated by the "no back up" system. The claim is also made that dehydration is more uniform throughout the block. So far no figures have been submitted to prove these two statements. It may be said, however, that the production is increased to a considerable extent by the use of this system, this increase being made at the expense of the quality of the product obtained. The effectiveness of the system depends entirely upon the care which is exercised by the operator and since a part of the technique of this new method consists in holding the alcohol for a definite time in the block, there would always be a tendency on the part of the operator to shorten this period of time with the consequent result of slurring the operation and of turning out an inferior block.

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The dehydrated blocks must be first thoroughly broken up before the next operation of mixing is commenced. For this purpose they are transferred into a rotating drum or block breaker, equipped on the inside with a wire screen and iron prongs. This barrel upon revolving throws the block against the prongs, thus breaking it into small lumps which lend themselves more readily to the mixing operation and which in turn insures a more even colloid.

From this point up to the time the powder is put into the solvent recovery the powder is kept in closed containers as much as possible between the various steps in the manufacturing process in order to prevent excessive losses in solvent, which is an important point, not only from the economical but also from the manufacturing standpoint.

Mixing.—The mixing operation is the second step in the formation of the colloid. As has been pointed out above, unless care is exercised during the dehydrating process in producing a block of uniform dehydration, it will be impossible to secure a good colloid. It is no less important that the ether be added to the mass in such a manner that the evaporating losses are minimized by incorporating the ether throughout the mass as quickly as possible. This is accomplished by the use of a mixing machine. It consists of a covered brine-cooled tank in which a double worm revolves, giving a kneading motion to the material in the mixer. With this worm in motion, the ether is added through a distributing plate in such a way that the evaporative losses are reduced to a minimum, but at the same time it is not added fast enough to jeopardize a proper mixing. In the case of the small arms powders and of the one pounder single perforated grains, graphite is added to the mixer charge before the ether is run in, and it is sometimes the practice to set aside one set of mixers for graphited powders.

It is also at this stage of the process that the so-called stabilizer is incorporated into the colloid. The material used for this purpose is diphenylamine, and there is dissolved in the ether enough of this substance so that the finished powder will contain between 0.40 and 0.50 per cent diphenylamine.

The object of adding diphenylamine at this stage is to thoroughly incorporate it throughout the colloid so that on long continued storage any nitrous fumes which may be evolved from the powder will be absorbed by this so-called stabilizer. The many factors entering into the use of this material are more properly discussed in a later chapter on surveillance and stability.

Pressing.—The colloid is next subjected in sequence to the action of a preliminary press, a macaroni press,[1] and a final blocking press.

[1] Since the writing of the above, the use of the macaroni press has been abandoned, the same object being accomplished now at all plants by means of one or more 10–20 mesh steel wire plates inserted in the graining press between the 35 powder block and the die plate.

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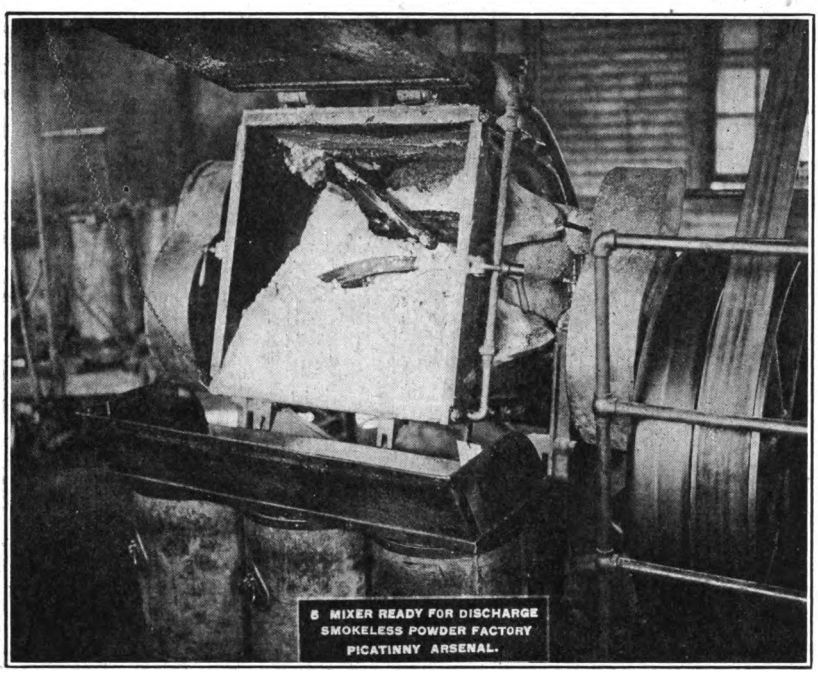

PLATE 16.

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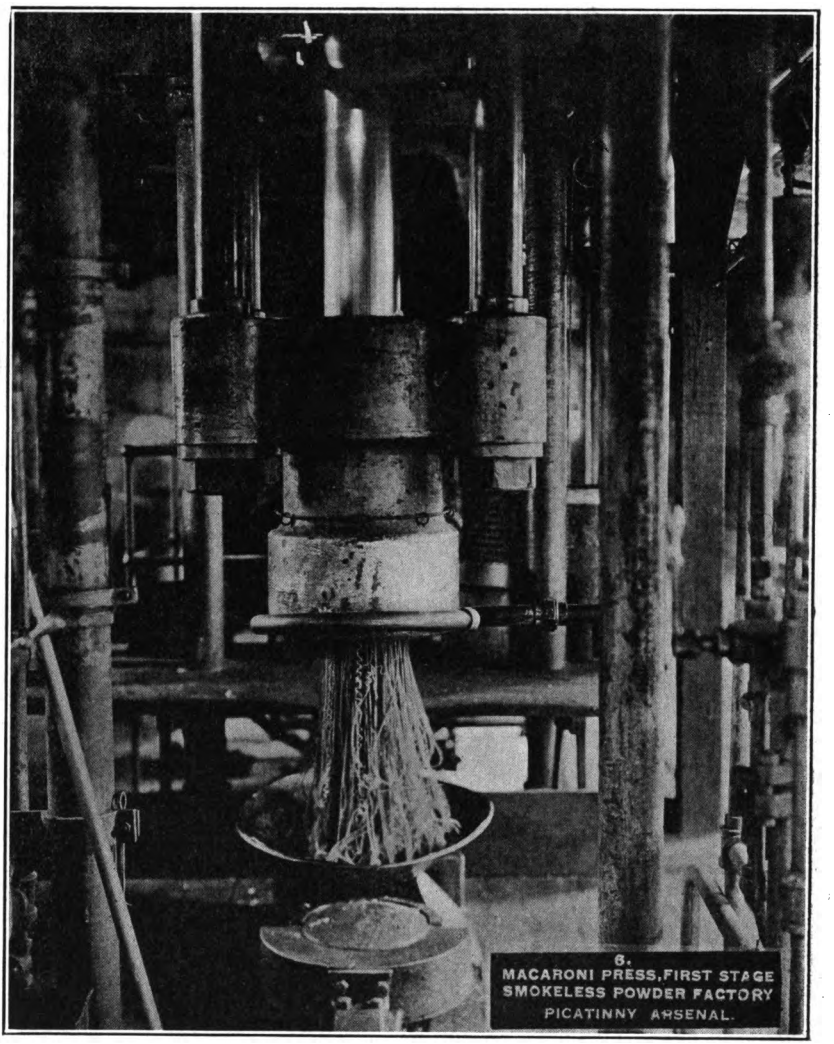

PLATE 17.

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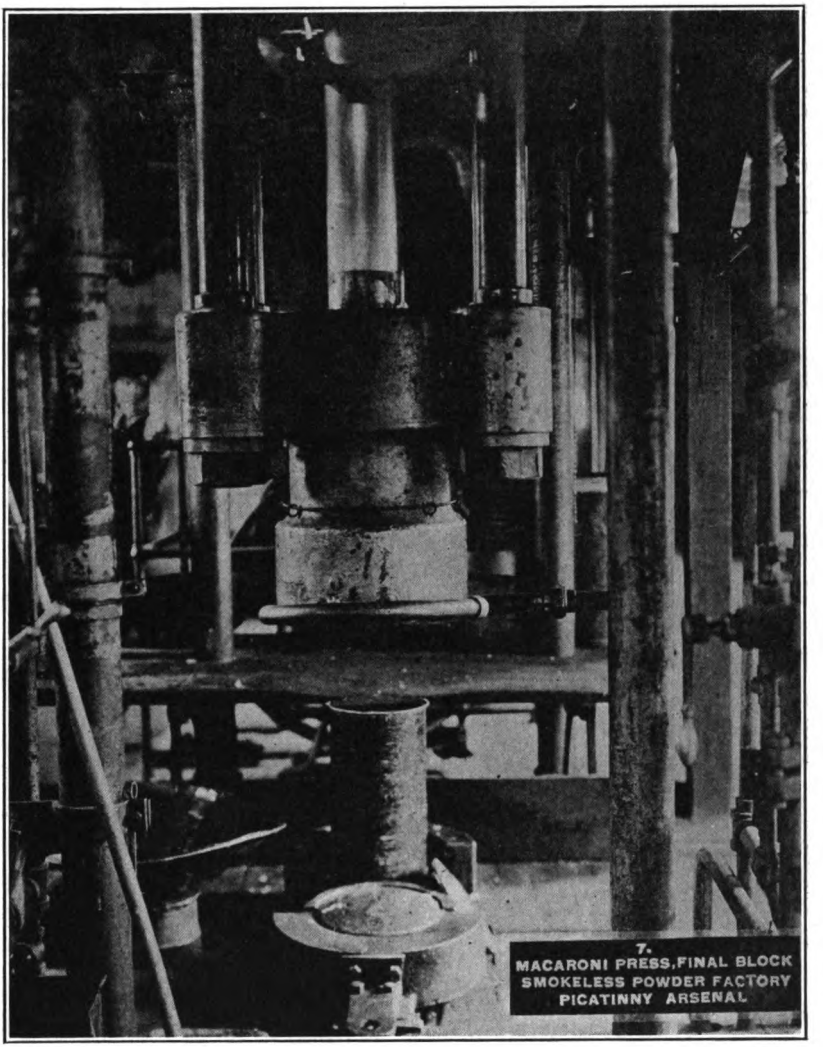

PLATE 18.

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PLATE 19.

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The incorporation of ingredients as accomplished in the mixing is really but a preparatory stage for the final formation of the colloid, this last step being completed by the action of the presses.

The preliminary blocking press consists merely of a cylinder and piston similar in action to the dehydrating press. It forms the colloid into a dense cylindrical mass by subjecting it to a compression of 1,800 pounds per square inch. This "preliminary block," so called, is then transferred to the macaroni press. The operation here consists in straining the solid block of colloided matter through a heavy brass screen and at a pressure of 4,800 pounds per square inch, in such a manner that the material as it is ejected is similar in appearance and size to macaroni. As it leaves this press it falls by gravity into the hopper of the final blocking press. This is similar in every respect to the preliminary blocking press and forms the colloid into the final shape before it is taken to the graining press. The block is here subjected again to heavy pressure for exactly three minutes, thus completing the colloiding of the pyro cotton. The colloid now is entirely different in appearance from the material as drawn from the mixers, for it has been changed from a mass resembling damp sawdust to a dense, elastic, dark brown substance. These operations of pressing insure, to the greatest possible degree, a uniformly thorough action of the solvent upon the pyro, and very nearly eliminate the possibility of having uncolloided cotton in the finished powder.

Graining and cutting.—The final operation from the standpoint of the granulation of the powder occurs in the graining press room. These presses may be set either horizontally or vertically. Their action is to force the colloid through a steel die, shown in accompanying figure, in such a manner that the expressed material, which takes the form of a string, will be delivered at a uniform rate of speed under the control of the operator at the press. The power which is necessary to force this colloid through the die is very great and is supplied by means of a hydraulic ram, under a pressure of 2,500 to 3,800 pounds. The press head may be equipped with one or more barrels, depending upon the rate of production of the colloid from the other departments and also upon the capacity of the graining presses themselves. When small arms powder is being grained there may be 50 strings issuing simultaneously from the head. With a large caliber powder, however, such as 16-inch gun, it is customary to use but one barrel, or at the most two. The "powder" issues from the press head in the form of a flexible rope which is led over pulleys to a cutting machine. This cutting machine is capable of very fine adjustment and is so manipulated that the ratio of the diameter of a grain to its length always remains constant.

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The factors affecting the size of the grain and its relation to the type of gun for which it is designed are discussed in a subsequent chapter.

Solvent recovery.—Having prepared the powder in a definite form of granulation the next step is that of recovery of the ether and alcohol which is given off during the process of drying. The unit which is concerned in the recovery of this solvent is termed the solvent recovery, and may consist of any one of three types: First, the chamber type of solvent recovery, in which the powder is transferred from a car to a small galvanized iron box set in an air-tight chamber; second, the car type of solvent recovery, in which the car itself containing the powder grains becomes the chamber; and third, the can type of solvent recovery. In all of these the governing principle is the same.

Warm air is circulated through the powder and is then forced over cold coils. This change in temperature causes a precipitation of the solvent upon the coils and produces, in effect, a miniature fog. The saturated air after passing over these cold coils loses its surplus solvent, is reheated and then is again forced through the powder in continuous cycle, in this manner completing the closed system of ventilation. The length of treatment depends upon the size of the powder; the larger calibers, of course, requiring a greater length of time than the smaller ones. Definite rules are laid down governing the length of time necessary for powder to remain in the solvent recovery building—rules which are the result of experiments and which combine the maximum of efficiency with the best results from the standpoint of drying.

Drying.—There are three separate types of drying operations: The first and most satisfactory, except from the standpoint of time, is the air dry. A second method, known as the water dry system, has a great advantage as to time saving, and up to the present time there is little reason to believe that the resulting powder is not as satisfactory as that dried by the air method. Finally, a new process, termed the Nash alcohol dry system, appears at the present time to have unlimited possibilities from all standpoints. It is also the more logical from the chemical standpoint, for the main difficulty in the drying of smokeless powder consists in the elimination of the ether rather than the alcohol from the colloid. This is more readily accomplished by alcohol than by either water or air, as used in the first two methods.

Air dry treatment.—In this treatment the powder is transferred directly from the solvent recovery house to the dry house and placed in bulk in large bins. The temperature is raised after a time and maintained as high as 45° C. These bins are narrow, so as to give

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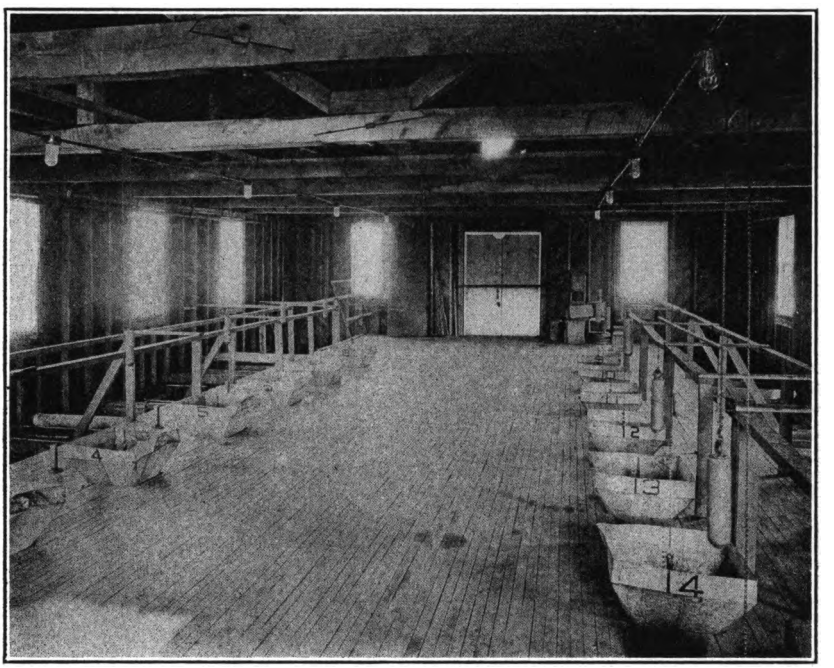

PLATE 20.—CHARGING FLOOR, CAN TYPE, SOLVENT RECOVERY HOUSE, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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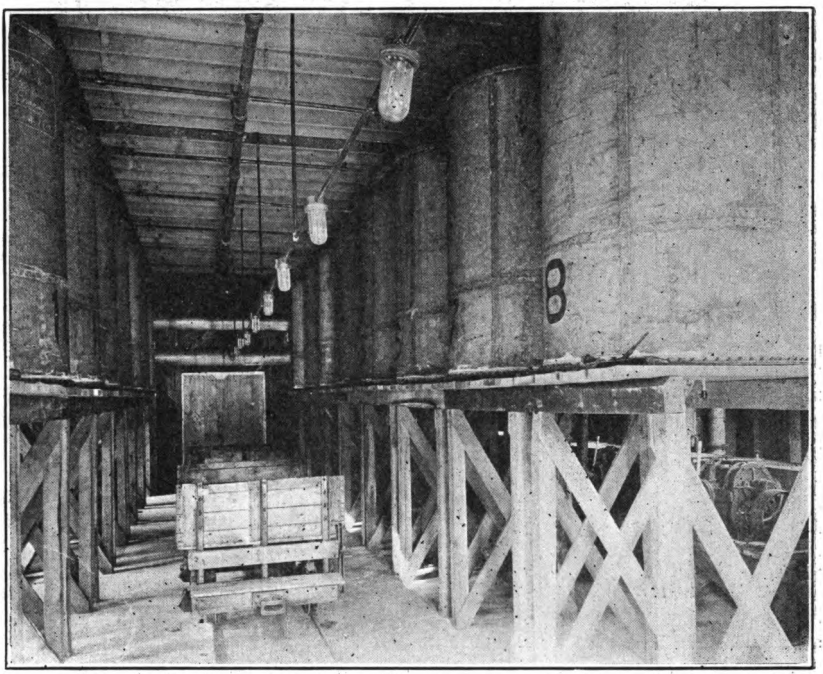

PLATE 21.—CAN AND DISCHARGE FLOOR, CAN TYPE, SOLVENT RECOVERY HOUSE, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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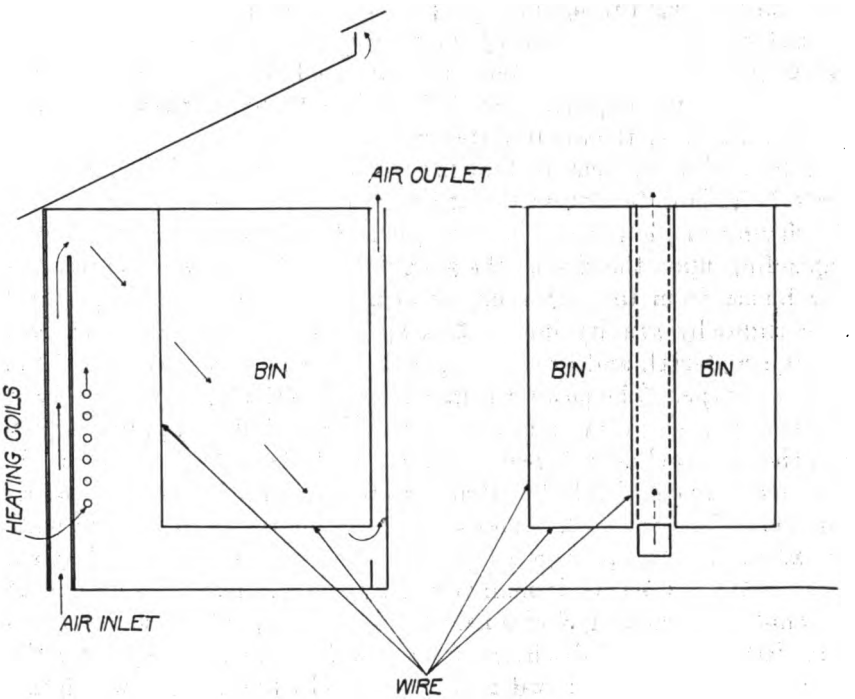
a relatively thin cross section, to insure an even distribution of heat throughout the mass of powder. From time to time the laboratory analyzes a sample of the powder to determine if the required moisture and volatile content has been reached. This moisture and vola-

SCHEMATIC SKETCH OF
NO'S. 3 AND 5 DRYHOUSES.

CIRCULATION.



ARROWS SHOW COURSE OF
AIR CIRCULATION.

PLATE 22.

tile content, or total volatiles, as it is sometimes called, is very important from the standpoint of ballistics.

Smokeless powder is, to a certain extent, hygroscopic. Extensive experiments have been performed for many years to determine definitely the amount of total volatiles necessary in a certain size powder to give the best results. If the powder is permitted to become too dry, a small weight of charge with correspondingly large air space will be encountered in the test firings in the gun, resulting in ex-

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cessive pressure at service muzzle velocity, owing to too rapid combustion. If, on the other hand, it is not dry enough a relatively high weight of charge with correspondingly small air space will result in excessive pressure at service muzzle velocity. It is, then, very necessary that the drying operation be carefully watched from the standpoints of chemical control and of technical manipulation of the house.

Water dry treatment.—The main difference between the air dry process and the water dry process is the difference in the surrounding medium. In the first case it is warm air, and in the second warm water, but the object desired is the same in either case. Water is kept circulating throughout the powder at temperatures which are at first relatively low, but which are subsequently raised to 55° C. Later the powder is removed and air dried for a short time; this latter treatment requiring much less time to finish than when the powder has only the air dry treatment.

A later development in this process is the so-called "continuous drier." This differs from the ordinary dry house treatment in that the drying of the powder is accomplished in between 4 and 5 hours, depending upon the size of the granulation. The powder enters the dry house from the water dry system, is hoisted to a hopper and then slides by gravity into a shaking screen. This screen removes foreign material, and drops the powder to a bucket conveyor of the ordinary type. The powder is then hoisted to the top of the building, where it is thrown into a drying chute. This chute is approximately 6 inches in thickness, 5 feet in width, and about 10 feet in length, and is equipped with baffles running crosswise in the direction of its smallest dimension. A series of screens on the side wall provide the means for the passage of warm air through the powder; and a temperature of 50° C. is maintained by this means at the bottom of the chute. A shaking device near the floor is capable of such regulation that the rate of discharge from the drier, and consequently the volatile content of the powder, is controlled by the speed at which this shaker is operated and by the amount of clearance between the shaker and the bottom of the chute. In one of the largest plants one continuous drier is capable of drying to the correct moisture and volatile content 100,000 pounds of 75 mm. powder in 24 hours.

Alcohol dry treatment.—In the Nash alcohol dry system the drying medium is a mixture of water and alcohol. The relative percentage of the two liquids varies according to the caliber of the powders, and experimental work is still being carried out to determine the best working conditions. If too strong an alcohol is used, it results in a brittle powder, a powder in which the external moisture is reduced to a very small amount, and one in which the shrinkage alters to a considerable extent the web dimensions. This naturally gives excessive

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PLATE 23.—EXTERIOR OF "CONTINUOUS" PROCESS DRY HOUSE, OLD HICKORY POWDER PLANT, NASHVILLE, TENN.

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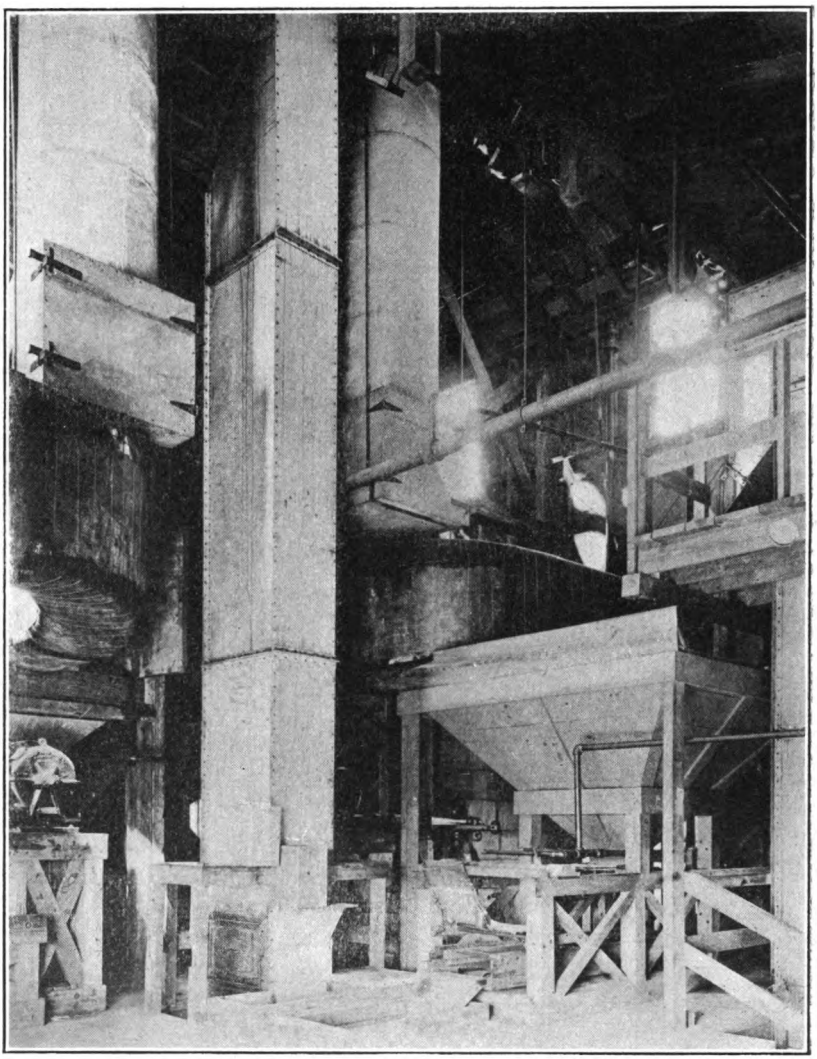

PLATE 24.—INTERIOR OF "CONTINUOUS" PROCESS DRY HOUSE, OLD HICKORY SMOKELESS POWDER PLANT, NASHVILLE, TENN.

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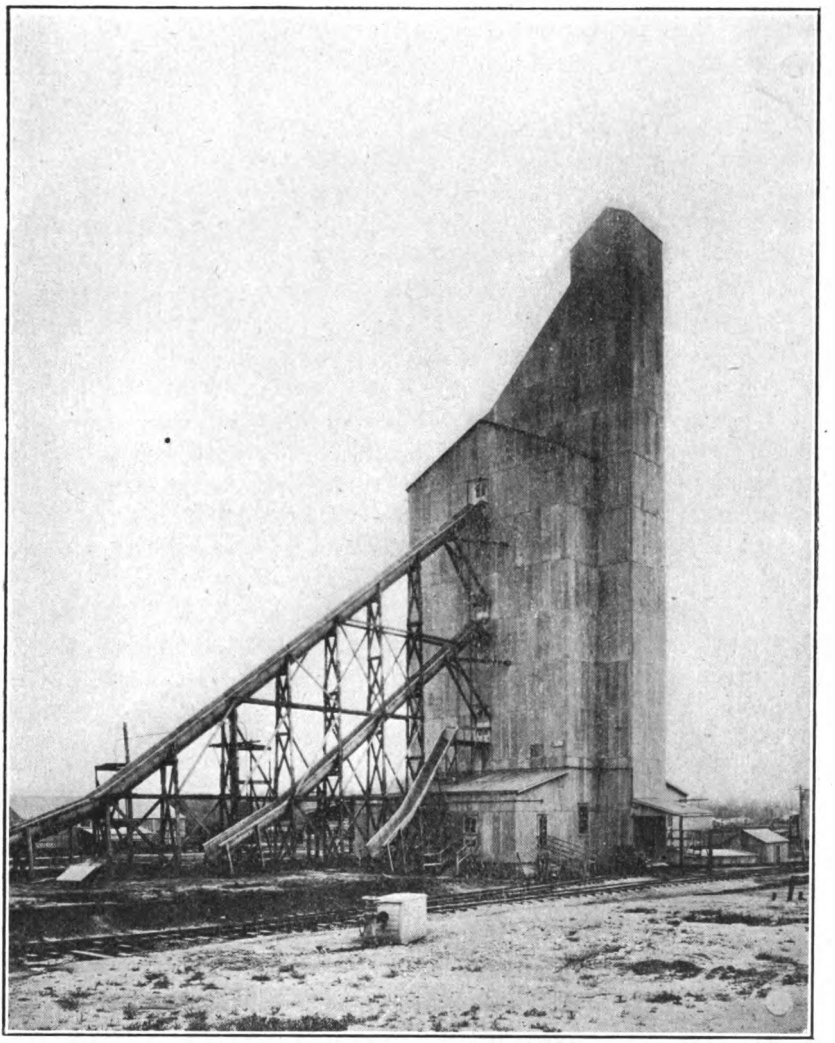

PLATE 25.—CANNON POWDER BLENDER, OLD HICKORY SMOKELESS POWDER PLANT, NASHVILLE, TENN.

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pressure in the gun. If too weak an alcohol is used, the time of drying is proportionately lengthened. This alcohol dry system has the advantage, that none of the ether is lost and but a very small part of the alcohol. It also does away with the solvent recovery treatment and it is only necessary to put the powder in the air-dry house for a short space of time to obtain the correct percentage of total volatiles, or to finish with a water-dry treatment and final drying in the continuous drier.

Blending.—The next step and perhaps the most important one from the standpoint of uniformity of firing is the proper mixing or blending of a certain arbitrary amount of powder. For the larger caliber guns it is customary to blend or mix either 50,000 or 100,000 pounds of powder, but for the smaller caliber powders, particularly for the small arms powders, lots ranging from 15,000 to 50,000 pounds are more usual. The blending operation consists merely in the transference of the powder by means of gravity from one bin to another bin, this transference resulting in a thorough mixing of all of the lot. These bins are so constructed that when full of a lot of powder the powder assumes the shape of a double cone with one apex pointed down toward the discharge pipe and the other apex pointed up toward the top of the bin. The proper construction of these bins from the standpoint of the correctness of the angles at the sides of the bin is very important. If the sides of the bin are too steep the powder will slide down toward the apex of the lower cone. If, on the other hand, the sides are built on too gradual a slope the powder will not flow freely from the bin and it would be necessary to use a raking device in order to empty the bin toward the end of the lot. It is essential, therefore, that a point midway between these two be found, a point so selected that the powder will not slide down the side of the bin, yet at the same time will insure a complete emptying and mixing of the lot. These angles have been determined and when the principles are observed no difficulty results from lack of proper blending. After two or three cycles from one bin to the other have been completed, the powder is weighed and boxed.

A new type of blender has been worked out at Picatinny Arsenal, which apparently is a considerable improvement over the old "tower blender." In the place of two bins set one upon the other as in the old type, an awkward arrangement which necessitated a building at least 100 feet high, two separate buildings were constructed about 100 feet apart. The bottom of the one bin is connected with the top of the other by an endless belt. There are, then, two belts operated independently of each other for the transference of the powder from the bottom of one bin to the top of the other. The arrangement at the bottom of each bin is such that the powder may be boxed in either building. When it is desired to

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empty one bin and transfer to the other for the purpose of blending, it is merely necessary to put the belt in motion and open the chute.

The speed of the belt is such that 100,000 pounds are hoisted in 40 minutes, a speed not possible with the older type of blender. This blender requires but one man to operate, whereas with the other type it was necessary to have about 10 men. The fire risk also is reduced to a minimum, for in case one building should take fire, a series of water curtains within the shed over the belts would confine the blaze to its point of origin.

After the blending is completed the lot of powder is boxed and stored. The powder container used for storage is merely an air-tight zinc box about which is built a wooden box completely covering and protecting the metal inside. It is of such a size as to hold from 110 to 140 pounds of smokeless powder, depending upon the type of box. These boxes are tested for air leaks to insure the powder retaining the same moisture and volatile content as when withdrawn from the dry house.

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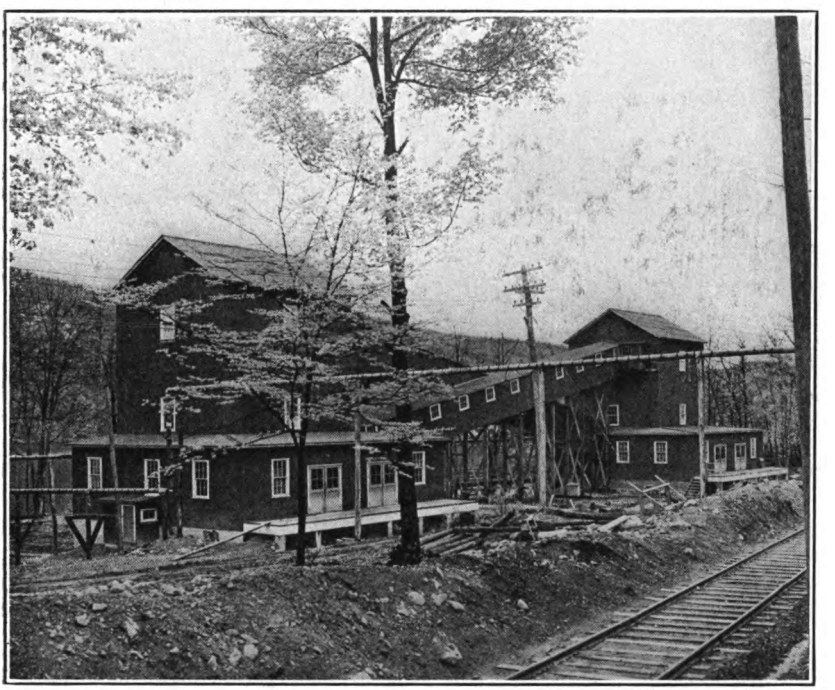

PLATE 26.—CANNON POWDER BLENDER, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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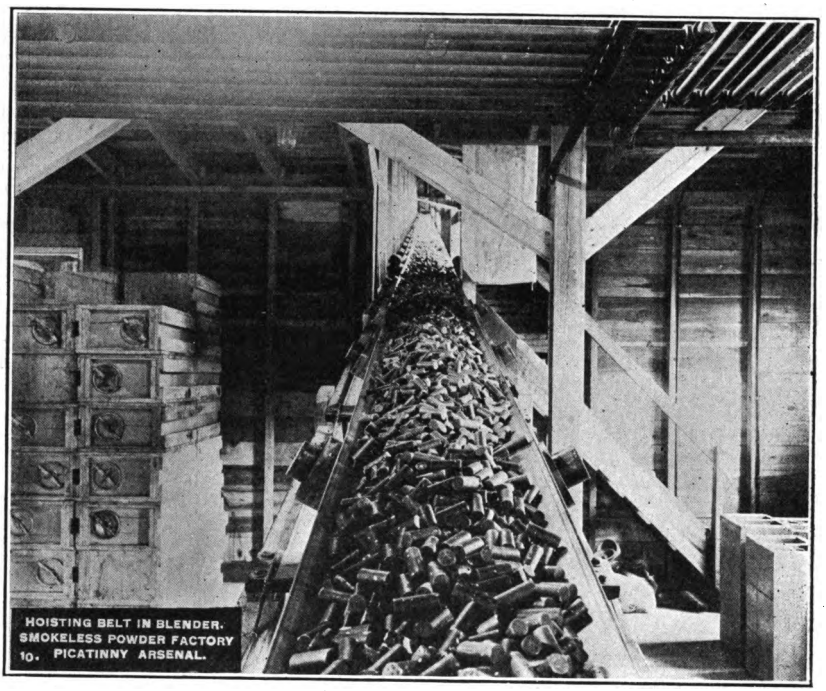

PLATE 27.

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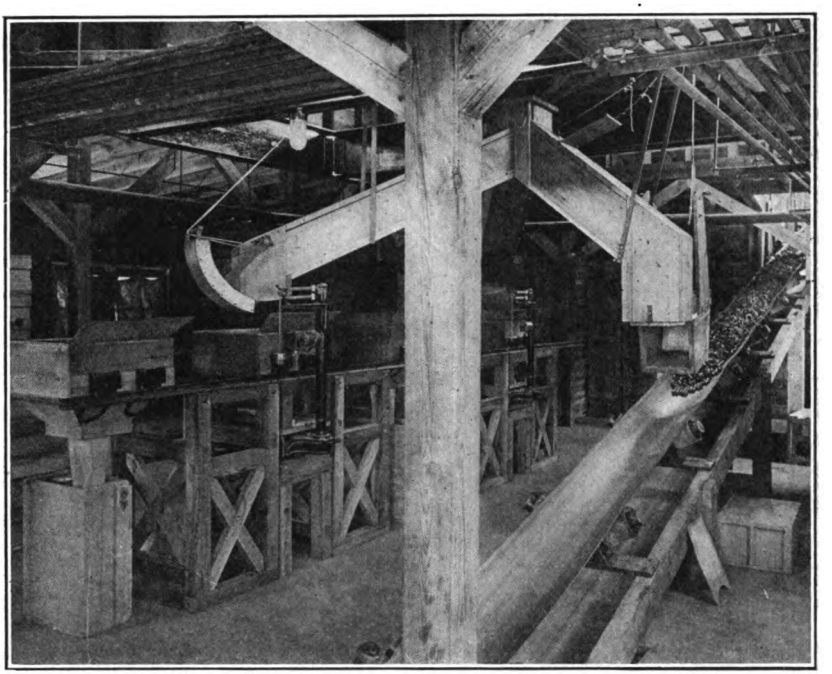

PLATE 28.—BOX FILLING AND WEIGHING FLOOR, CANNON POWDER BLENDER, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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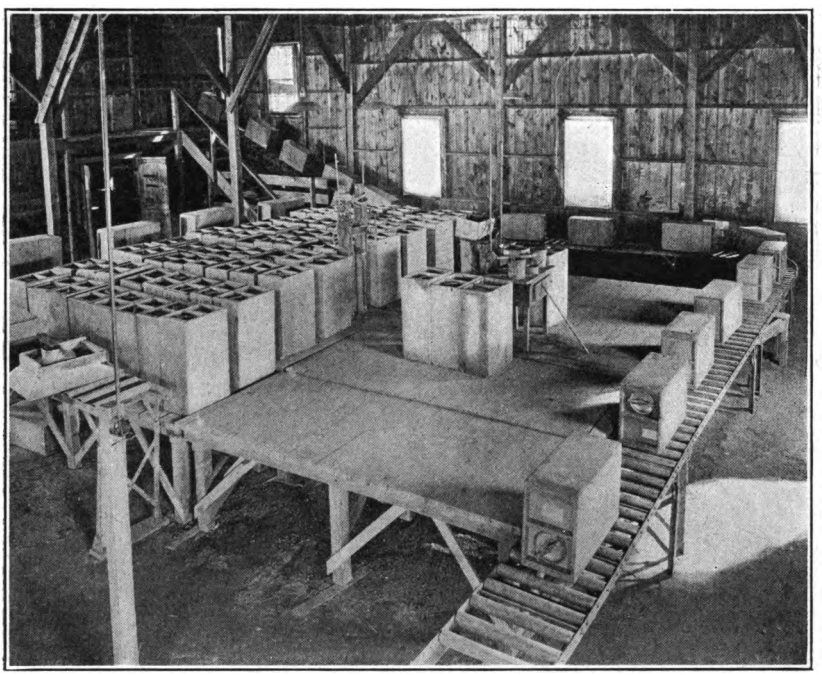

PLATE 29.—POWDER BOX TESTING HOUSE, SMOKELESS POWDER FACTORY, PICATINNY ARSENAL, N. J.

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CHAPTER II.

GRANULATION OF SMOKELESS POWDER.

GENERAL.

The propellant used as a charge for the gun possesses a certain force or latent power which upon combustion becomes a kinetic or moving force and which drives the shot to the muzzle of the gun. That which actually occurs when powder is ignited is as follows: In the first place, the powder is converted by change of state, i. e., from solid to gas, into a volume greater than that originally occupied by the powder; in the second place, the heat generated by the explosion expands the volume of this gas and increases its pressure. Since the pressure of the gas is equal in all directions, the expansion will naturally follow the line of least resistance, thus setting the projectile in motion.

The rapid development of the gas pressure within the gun should be of such a progressive nature that the force exerted should not attain its maximum at the time of the ignition (as would be the case if a high explosive were used as a propellant), but rather should attain it by a relatively gradual rise. The control of this pressure lies in the form of granulation of the individual powder grains. This granulation determines the area of the burning surface of the grain, which in turn controls rate of combustion, and through that, the pressure.

A brief consideration of the factors influencing and determining the proper granulation of the powder will involve a discussion, first, of the best form of the powder grains, and second, the factors which influence the size of the grains.

The best form of granulation from a ballistic point of view is, first, that which with the smallest given weight of charge will impart to the projectile the highest muzzle velocity within the prescribed limits of maximum pressure; second, that which will cause the minimum erosion to the bore, and third, that which shows maximum regularity in ballistics. The grains should burn uniformly from the surface and the rate of burning should vary directly with the pressure; the greater the burning surface, the higher the pressure, other things being equal. It is evident, therefore, that the shape of the grain is a direct factor in determining the amount of burning surface.

Shape of granulation.—When the powder is ignited its rate of burning is dependent upon the area of the burning surface. It was formerly supposed that the powder grains should be so designed

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that this area should remain nearly constant, in an attempt to maintain the original pressure developed upon ignition throughout the period of combustion.

Powder was made in the form of tubes, broad tapes, and thin flakes as the result of efforts to realize this condition. This theory, however, is not in accord with the practice in this country, and it has been demonstrated that instead of maintaining a constant pressure during the combustion of the charge, the pressure should be gradually increased until the maximum is reached, in the case of the ideal gun, at the time that the projectile is about to leave the muzzle. Our guns are designed to withstand a pressure increasing to the maximum at a point in the bore just ahead of the powder chamber. If this object is to be attained there must be an actual progressive increase in the area of the burning surface. This larger area may be secured either by altering the shape of the grain (for example, from a true cylinder to a square form, or better, to the Walsh grain), or else by perforating the grain longitudinally, with holes so spaced that the progressive burning of the grain increases the area exposed to ignition. This multiperforated grain has been manufactured in three shapes, namely, the cylindrical grain, the square grain, and, lastly, the sliverless or Walsh grain. Of these three, however, the cylindrical form has been the most used. The cylindrical or multiperforated grain for cannon powder has seven circular longitudinal perforations, one central and the other six equally distributed midway between the center of the grain and its circumference. A uniform distance between the center of the central perforation, the center of the outside perforation, and the outside circumference of the grain itself is the object sought, since it has been found that this facilitates the complete combustion of the charge. The length of the dry grain is between 2.1 and 2.5 times the outside diameter. For the smaller type of gun the multiperforated grain finds no use, and in its place the single perforated grain has been adopted. The types of gun for which the single perforated grain is used are the .30 caliber rifle, 37-mm. gun, 2.95-inch subcaliber, 2.95-inch mountain gun, and 3-inch mountain howitzer. Unlike the multiperforated grain, it burns with practically a constant burning surface.

The square form of grain is made with four longitudinal ridges on each side and nine square perforations. Contrary to expectations, this grain has not proved satisfactory, first, because of the difficulties in cutting the die, and, second, because of the difficulties in maintaining the square shape of the grain, due to the soft, pliable nature of the colloid.

Another form of grain, the sliverless or Walsh grain, was invented by Col. J. E. Walsh in 1912, at Picatinny Arsenal. The following

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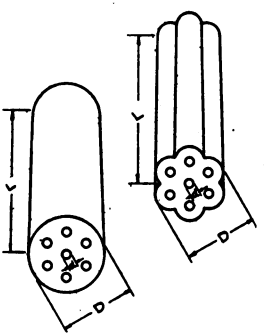
diagram shows a comparison of the burning surface of the cylindrical and sliverless grains. When the cylindrical grain is burned it can be seen that there still remains to be burned six inner and six outer pieces of powder of triangular cross-section called slivers. The Walsh or sliverless grain eliminates this defect, leaving no slivers when the powder in the charge is burned. This complete combustion of each grain of powder has a direct economic effect in that it reduces the weight of the charge, and also considerably accelerates the rate of incendition by increasing the surface per unit of mass.

Size of granulation.—In designing the granulation of the powder, the chemical composition of the colloid does not need to be considered, as it does not alter for the various types of guns. The factors which affect the size of the grain are, first, the type of gun for which the powder is to be used; second, the weight of charge; third, the



weight of the projectile; fourth, the effect of the per cent solvent upon the shrinkage of the powder; fifth, the effect of the moisture and volatile content of the powder; and lastly, the effects of the different methods of drying.

Artillery is divided into three general classes: guns, howitzers, and mortars. Tschappat (Ordnance and Gunnery, J. Wiley & Sons, New York, 1917) describes the following types of artillery:

Seacoast guns, field guns, mountain guns, anti-aircraft guns, and subcaliber tubes.

The howitzers are classed as mountain howitzers and field howitzers.

The mortars are seacoast mortars and trench mortars.

In comparing the three types of cannon as to length, the gun is the longest, its length ranging from 40 to 60 times the bore of the gun; howitzers are medium in length, and mortars the shortest. Therefore, the mortar type would require a powder with a larger burning surface than either a gun or a howitzer of the same caliber. The gun, however, as a class gives the highest degree of accuracy, permits the longest travel of the projectile, and imparts the highest muzzle velocity.

The calibers of seacoast guns range from 2.24 to 16 inches and are permanently mounted in fortifications. Field guns, or mobile artil-

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lery, are designed to accompany or follow an army in the field, and are smaller in caliber, except in some of the railroad mounts. Depending upon the type of the gun, however, the granulation of the powder must be so designed that the functions of the different guns are best served.

Howitzers are used only in mobile artillery. "For each caliber of gun there is designed a corresponding howitzer of an equal degree of mobility, and the caliber of each howitzer is the same as that of the gun of the next lower degree of mobility. That is, the howitzer corresponding in mobility to one of the guns is of the same caliber as the next heavier gun and uses the same projectile."—(Tschappat, *idem.*)

The seacoast mortars are short guns and in firing there is always a large amount of unburned powder slivers thrown from the muzzle, except when the sliverless or Walsh grain is used. This grain, as has been pointed out before, by providing a larger burning surface, burns quicker and thus eliminates this undesirable feature. Since each type of gun has its specified size of powder chamber, it is necessary to ascertain this capacity before designing the granulation of the powder. Other factors being equal, the greater the capacity of the powder chamber, the greater the size of the powder grains. If, for instance, the capacity of the powder chamber for the 12-inch mortar, model of 1890, is 2,674 cubic inches, and 12-inch mortar, model of 1912, 3,770 cubic inches, using the same weight of projectile (617 pounds) and approximately the same weight of charge, the "average web" for model of 1890 is 0.0642 inch (Lot P. A. 199–1916) and for model of 1912, 0.0768 inch (Lot P. A. 198–1916).

Effect of weight of charge.—When the weight of the charge is reduced there is a corresponding decrease in both the velocity and pressure developed on combustion. Within certain limits, however, this lowered weight of charge can be effected, without sacrificing the pressure, by altering the granulation of the powder. The dimension most to be considered in this connection is the "average web." By this term is meant the mean distance which constitutes the least burning thickness from the edge of one surface to the edge of the next surface in the diametric direction. A full discussion of the dimensions of the powder grain will be found under section "green dimensions, die dimensions, dry dimensions, and web measurements." To decrease the weight of charge the average web must be decreased, but this decrease invariably causes increase in pressure with service muzzle velocity; consequently there are limitations. From an economical standpoint the greatest efficiency is obtained when the desired muzzle velocity, with the maximum allowable pressure developed just as the projectile starts moving, is produced by the least weight of charge. From a technical standpoint the greatest efficiency,

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that is, the highest muzzle velocity with the same pressure, is obtained when the pressure increases as the projectile travels along the bore of the gun, until reaching a maximum at the muzzle; but in this case the powder efficiency is lowest.

Effect of weight of projectile.—The following general classification of projectiles is indicative of the various types which have been, or are, in service (of these the high-explosive shell, shrapnel shell, and gas shell have been used most extensively):

Solid shot, cored shot, high-explosive shell, shrapnel, canister, and gas shell.

An increased weight of projectile will result in an increased maximum pressure in the gas if the same muzzle velocity is to be maintained with the same powder, size of powder chamber, and length of travel.—(Tschappat, p. 518.)

The maximum pressure for any gun being fired, the use of a heavier projectile will usually require the use of a powder with a greater web thickness. Of two projectiles fired with the same initial velocity and elevation the heavier projectile will lose its velocity more slowly and will attain a greater range. For any given range it will be subjected for a less time to the action of gravity and other deviating causes, and will therefore have a flatter trajectory and greater accuracy. The advantages of the heavier projectiles are, therefore, increased range, greater accuracy, and a flatter trajectory.—(Tschappat, *idem.*, p. 517.)

Effect of solvent on shrinkage of powder.—It has been stated that a mixture of ether-alcohol is used as a colloiding agent or solvent for the nitrocellulose. The excess solvent which is always present is eventually dried out during the solvent recovery and the dry house processes, and used again for the manufacture of ether. Depending upon manufacturing conditions and the type of powder to be manufactured, the amount of solvent, in terms of dry weight of nitrocellulose, may vary from 80 to 105 per cent. For .30 caliber powder usually 105 per cent solvent is used; for reworked powders, 90 per cent; and for cannon powders, 100 per cent. An excess of solvent enables the powder to pass through the press more easily, but on account of the softness of the grains they will dry unevenly and often blister and split. On the other hand, too little solvent not only delays the incorporation, but is likely to interfere with the perfect homogeneity of the powder.

The per cent solvent used is nearly of as much importance from the ballistic standpoint as are the dimensions of the powder grains; in fact, this percentage influences, to a great extent, these measurements, for the greater the amount of solvent, the greater will be the shrinkage of the drying powder.

Effect of moisture and volatiles.—After graining, the bulk of the solvent is dried out, but 2 per cent to 8.5 per cent may remain in the powder as moisture and volatiles or total volatiles, the amount depending upon the size of the grain. No better description of the

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effect of moisture and volatiles can be given than the following from Tschappat's "Ordnance and Gunnery" (*idem.*)

The alcohol used in the solvent contains 5 per cent water, which generally remains in the powder after drying. Additional water may be absorbed from the air during the process of manufacturing and handling. Recent lots of powder also contain 0.4 to 0.8 per cent of a stabilizer, and .30 caliber rifle powders contain, in addition, 1 per cent of graphite.

Smokeless powder may, therefore, be considered to be a mixture of nitrocellulose, alcohol, water, and sometimes a stabilizer and graphite. Most of the ether used is evaporated out during the drying process.

From calculations it is found that the energy per pound of pure nitrocellulose of 12.60 per cent nitrogen is 1,422,000 foot-pounds per pound. If not, an inert material, that is, one that takes no part in the reaction at combustion, is mixed with the nitrocellulose and the energy per pound of the resulting material will be less than that of pure nitrocellulose. For instance, if 0.99 pounds of pure nitrocellulose of 12.60 per cent N is mixed with 0.01 pound of inert material, the inert material will be 1 per cent of the total weight and the energy per pound of the resulting material will evidently be $1,442,000 \times 0.99 = 1,427,580$ foot-pounds per pound.

Now, of the materials entering powder as given above, water is considered as having the same effect as the same percentage of inert matter. Alcohol has a greater effect than inert matter for the reason that the carbon contained in it combines with the CO_2 resulting from the combustion of the nitrocellulose, thus forming a larger quantity of CO and a smaller quantity of CO_2, than in the combustion of pure nitrocellulose. Theoretical considerations and practical tests indicate that the effect of 1 per cent alcohol in reducing the energy per pound of nitrocellulose is equal to the effect of 2.5 per cent inert matter.

In the same way the effect of 1 per cent stabilizer, which is higher in carbon content than alcohol, is shown to be equal to the effect of 4 per cent inert matter. Graphite, though entirely carbon, does not readily take part in the reaction and, therefore, the effect of 1 per cent graphite in reducing the energy per pound of nitrocellulose is considered equal to that of 2.5 per cent inert matter.

Consequently, the granulation of the powder must be so calculated that it will counteract the reduction of the energy of the powder by the solvent remaining after drying. In order to give more energy, the burning surface should be increased by diminishing the average web measurements or the size of the grain, or by changing the form of the grain.

Effect of methods of drying.—The methods of drying which have been previously described in the process of manufacture affect both the ballistics and the stability of a powder.

In the discussion of the alcohol dry system, mention was made of the fact that the strength of alcohol used influences, to a marked degree, the shrinkage of the powder. This shrinkage, however, can be regulated by varying the relative percentages of alcohol and water used in the process. While there is a tendency toward a greater shrinkage with alcohol-dried powder than with water-dried powder, the experiments at the present time seem to indicate that this factor will be easily controlled, since air-dried powders show the least amount of shrinkage. It is obvious that a larger allowance in measurements should be made for the powder which has the greatest shrinkage and, therefore, the die dimensions of the air-dried pow-

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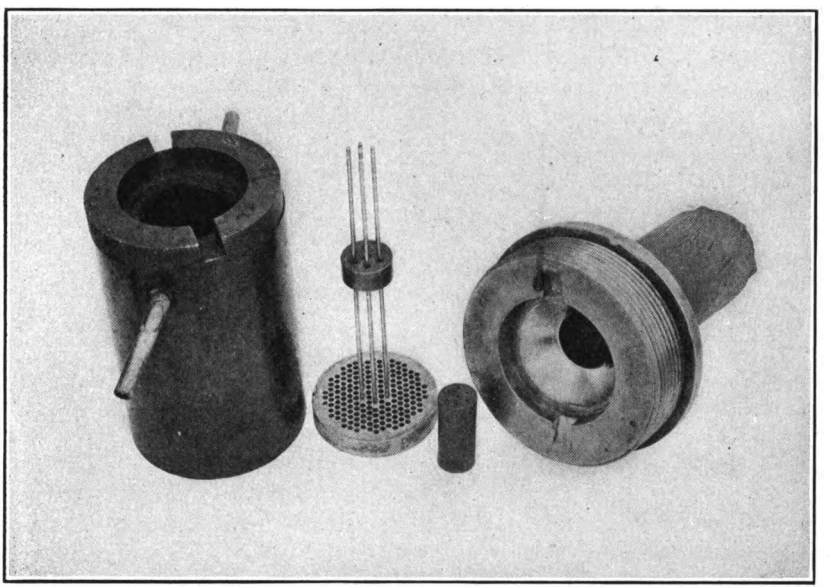

PLATE 31.—DIE BODY, PIN PLATE, PLUG, WATER JACKET, WATER-JACKET HEAD, AND SMOKELESS POWDER GRAIN FOR 12-INCH GUN.

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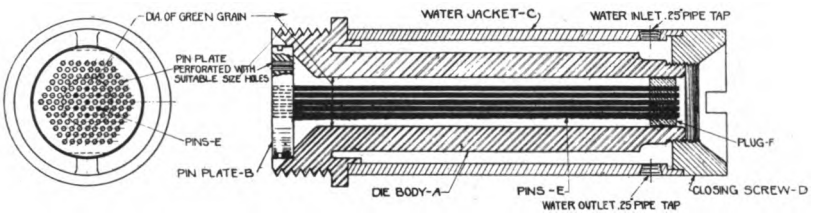
ders should be correspondingly smaller than those for the "water-dry" or "alcohol-dry" powders.

In considering the length of the powder grain in reference to its diameter it is known that if the green length is more than 1.875 times the green diameter, the grain will warp excessively and dry unevenly. On this account and in order that the grain may serve for convenient building into charges, as well as other factors, its length is limited. The requirement of prompt ignition throughout the length of the grain also limits this dimension, and by allowing 8 per cent shrinkage in length, and 30 per cent shrinkage in diameter, this will make the length of the dry grain a little less than two and one-half times the diameter. The per cent increase allowed should increase two-thirds per cent for every per cent increase in solvent.

Before designing the dimensions of the multiperforated, single perforated and sliverless grains, it will be necessary to understand the



POWDER DIE ASSEMBLY
USED FOR CYLINDRICAL GRAINS

PLATE 30.

following terms: Green dimensions, die dimensions, dry dimensions, and web measurements.

As the powder comes from the graining press it contains from 40 per cent to 50 per cent solvent and is called "green" because the solvent has not been extracted by the drying processes. The "green" powder has about the same dimensions as the steel die and pinplate through which it has just been pressed. The die body A consists of a steel block designed to hold the pinplate B, the water jacket C (having an inlet and outlet for water used for cooling the die while running the powder) and a closing screw D for the water jacket. The pinplate consists of a perforated plate, to which are attached the wires or pins E, which form the perforations in the grain, and the plug F, which holds the pins in place. The dimensions for both the die body and pinplate are called die dimensions.

It is necessary to calculate the dimensions of the die very accurately, as there are many factors which cause the measurements of the green powder to differ from those of the die. Among these factors is the spring of the pins (or needle wire) by which action the pins are drawn together as the powder is being pressed through the die, and which has the effect of decreasing the "inner web."

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Another factor is the consistency of the powder as it is being grained. The softer the powder, the more it will contract as it goes through the die, thus causing the green dimensions to be less than the die dimensions.

Dry dimensions.—Before the powder can be used, the solvent must be dried out so as not to leave over 8.5 per cent for the largest granulations and not over 2.5 per cent for the smallest granulations. The percentage of solvent is first reduced by the solvent recovery

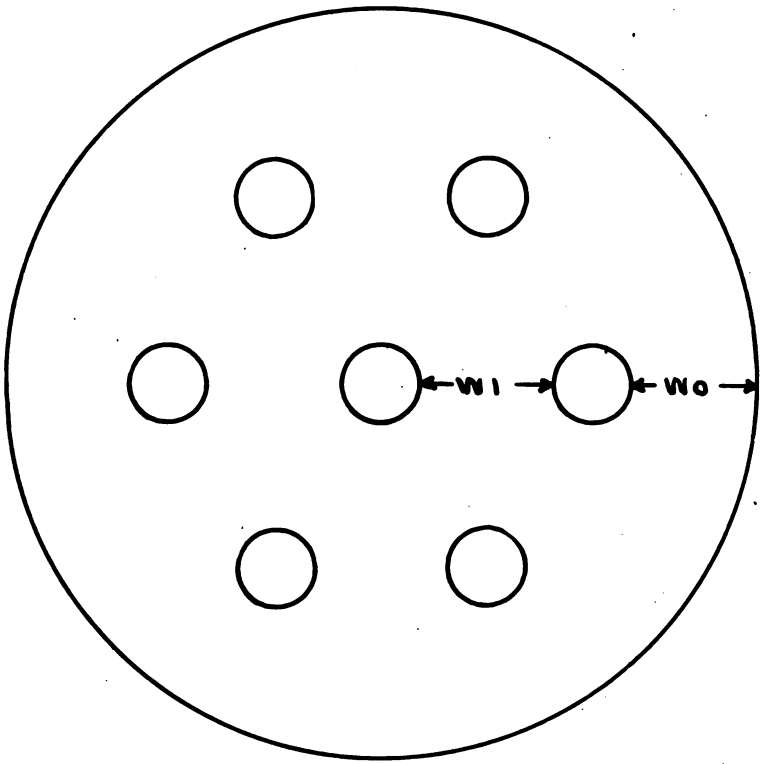

PLATE 32.—$Wa=\frac{Wi+Wo}{2}$.

process and finally by placing the powder in dry houses for a period of from 15 days for .30 caliber powder to three months or more for 16-inch powder. The powder is then blended and samples are taken for measurements and other tests. The measurements taken from the dry finished are called dry dimensions.

Web.—By the web of a powder grain is meant the minimum burning thickness, or the distance from the edge of one surface to the next surface in the diametric direction. There are three of these measurements: "Outer web," "inner web," and "average web." The outer web is the distance from the circumference of the grain to the nearest edge of the outer perforation. The inner web,

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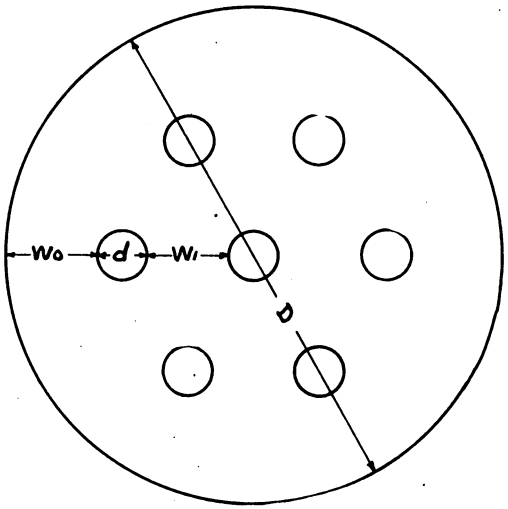
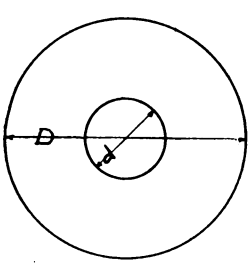
found only in multiperforated grains, is the distance between the inner edge of the perforation midway between the center and the circumference, and the nearest edge of the central perforation. The average web is found by adding two inner webs, two outer webs, and dividing by four. The symbol used for outer web is W_o, for inner web W_1, and for average web W_a. The average web is given as a basis for all other computations, and the purpose of the following calculations is to indicate the procedure used in computing the measurements for a die, from a standard average web measurement.



CYLINDRICAL GRAINS. 7 PERFORATIONS.
Dry Dimensions (Approx.)
$D = 10\,d$
$W_o = 5\% + W_1$
$W_a = \frac{W_o + W_1}{2}$
D = outside diameter
d = diameter of perforation
W_o = outer web
W_1 = inner web

To calculate an entirely new average web for the powder of a new gun requires a knowledge of interior ballistics and explosive theories, which is not within the scope of this book. An excellent and detailed explanation for calculating a new powder is given in Tschappat's Ordnance and Gunnery, Chapter IV.



CYLINDRICAL GRAIN SINGLE PERFORATION.
Dry Dimension, $D = 3d$
D = outside diameter.
d = diameter of perforation.

PLATE 33.

The calculation on the average web, which will be discussed, involves merely the change of the die measurements which may be made in order to conform to the different processes of manufacture, and to create better ballistic results for a new lot of powder.

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Perforation.—The perforation or pinhole of a powder grain is the hole in both single and multiperforated powders made by the needle wire of the pin plate. The diameter is always the required measurement of the perforation and is expressed by the symbol "d."

Diameter.—The capital D signifies the outside diameter of the grain, passing through its center and terminating in its circumference. In the multiperforated grain it includes three perforations and is calculated mathematically as the sum of two outer webs, two inner webs, and three times the diameter of the perforation or $D=2W_o+2W_i+3d$.

Needle wire.—Needle wire consists of steel rods, set in the pin plate as shown in the diagram, and which form the perforations in the powder as it issues from the die head. There are standard sizes of needle wire usually kept in stock at the factories, and the calculations of the die can be made to conform to the standard needle wire.

Pin circle.—The pin circle is formed by drawing a circle through the center of the six outer perforations. The diameter of the pin circle is calculated as the sum of the two inner webs and the two diameters of the perforation. This equals $2W_i+2d$. The pin plates are classified according to the diameters of the pin circles.

Slope of cone.—The powder is pressed through the die at a given angle and it depends on the consistency of the colloid whether the powder should be fed to the press slowly or quickly; for cannon powder the angle at which the colloid enters the die should be about 45° and for small arms about 30°.

Quick powder—Slow powder.—Wise (Gunnery, J. C. Wise, Johnson Publishing Co., Richmond, Va., 1912) gives the following definitions of quick and slow powders: "A powder with greater initial surface than the standard powder—that is, a powder of smaller granulation, will produce a greater maximum pressure and therefore will be a quick powder for the gun, and a powder of larger granulation will be a slow powder." Another factor to be considered in this connection is the percentage of "total volatiles." The higher this per cent the slower the powder, and the lower the pressure for a given density of loading; and conversely, the lower the per cent, the quicker the powder, and the higher the pressure for a given density of loading.

Calculation of average dry web.—The basis for all calculations of powder dimensions is the average web of the dry powder. As has been pointed out, the factors affecting this dimension include the percentage of solvent and the method of drying the powder. There are relatively wide variations in practice by the different manufacturing companies—variations which are necessitated by the differences in manufacturing technique, as well as by climatic conditons. Although the maximum temperatures of air drying and water drying

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are specified, the contractor is given enough leeway to insure a maximum speed of drying without injury to the grain. In other words, as long as the finished powder meets the required specifications, the minute details involved in the manufacturing process are of little consequence. Each company issues a description sheet which indicates both the die and dry measurements. For determining the best average dry web, it is necesasry to take the dimensions of the powders which have been given the best ballistic results. This information is obtained from an examination of the firing records, charge, velocity, and pressure curves, and if these are not available, the average dry web of any accepted powder can be taken as a basis. It is the average web of the die that is difficult to calculate because that measurement takes into consideration all the processes of manufacture, such as per cent solvent used, method of drying, moisture, and volatiles, etc.

Calculation of required dry dimensions.—When the average web has been determined and complies with the standard dimensions, the next step is to determine, theoretically, the other dimensions of the dry powder—that is, the outer web, the inner web, the diameter of perforation, the outside diameter and the length. The outer web is calculated as 5 per cent larger than the inner web. This is found by dividing the average web by 0.975 to obtain the outer web, and by dividing the average web by 1.025 to obtain the inner web measurements.

The diameter of the small perforation (d) is determined from the following formula:

$$\frac{d=4Wa}{7}$$

Theoretically, the outside diameter (D) equals ten times the diameter of the small diameter, or $D=10d$. In order to check this, another formula is used:

$$D=2W_o+2W_i+3d.$$

The length of the dry grain is calculated as two and three-eighths to two and one-half times the outside diameter (D).

The dry dimensions for a single-perforated grain are calculated differently. As there is only one web measurement, the outer web is the same as the average web and also the same as the diameter of the perforation (d). This would make the outside diameter (D) equal three times the average web, or

$$D=3d.$$

The dry length of the single-perforated grain is equal to three times the outside diameter, or

$$L=3D.$$

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Calculation of per cent shrinkage.—When all the above required dry measurements have been calculated and before the dimensions of the die can be determined, it is necessary to find the per cent of shrinkage for the average web measurement. This is very difficult to determine accurately because so many factors influence the amount of shrinkage. It has been stated that the greater the amount of solvent used the greater the shrinkage. An increase of two-thirds per cent shrinkage is allowed for every per cent increase in solvent. Air-dried powders have a smaller per cent of shrinkage than either water or alcohol dried powders. The per cent shrinkage of the multiperforated grain varies from 25 to 35 per cent. This shrinkage can also be determined by reference to the shrinkage of powder of other manufacturers, as noted on the description sheets, but care must be taken to consider the processes employed (such as solvent, drying, etc.), which affect equally the shrinkage.

Calculation of die dimensions.—When the per cent shrinkage for the average web has been determined, the next step is to calculate the average web of the die. It is found by the formula—

$$\text{Average web of die} = \frac{\text{required dimensions of dry grain}}{1 - \%\ \text{shrinkage allowed.}}$$

The result of this calculation gives the basis for the calculation of the other dimensions of the die such as W_o, W_1, d, D, and L. The same procedure is employed as described under the dimensions of the dry grain. These results are only preliminary and are not, in any sense, arbitrary measurements, for the inner and outer web measurements are always changed. The inner web of the die is often designed to be larger than the outer web, which is contrary to that required in the dry powders, for the reason that the spring of the pins as the powder presses through the die decreases the inner web thickness. Since the inner web thickness of the die, as shown in the records, shrinks more than the outer web, the inner web should be the larger of the two. But in some cases, however, the die dimensions of the inner and outer webs are the same, due to the varying factors in the manufacturing processes. In fact, there is no specified rule for finding the percentage of difference between the two measurements of the die. It must be found either by reference to other dies made for the same powder, or through experience in manufacture. Other dimensions of the die may also be changed to meet existing conditions. If, for instance, there is needle wire in stock which is 0.001 inch at variance to the designed die, the calculation for the diameter of the perforation (d) may be altered to conform to the needle wire on hand. It is, therefore, impossible to arrange any ar-

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bitrary rules for die calculations because of the various differences in drying processes and shrinkages.

Thus far there have been calculated the die dimensions for a tentative granulation. The next step is to find the per cent of shrinkage between the die and the dry dimensions. This shrinkage is found by using the formula—

$$\% \text{ shrinkage allowed} = 1 - \frac{(\text{required dimension of dry grain})}{(\text{dimension of die}).}$$

If this shrinkage does not seem to be within reason or within the prescribed limits, it must be changed to conform with the actual shrinkage of similar powders. Changing the shrinkage changes the die measurements and these figures must be changed again to conform to the formulæ and specifications until a satisfactory die with satisfactory calculated shrinkage is obtained. It is best not to change the required dry dimensions unless absolutely necessary, and in any case the average web of the dry dimensions must not be changed.

Measurement of green powder.—After the dimensions of the die have been calculated, the drawings made, and the die bodies and pinplates manufactured in the machine shop, the next measurements are those of the green powder at the time it is being grained. This is very difficult of accomplishment, as the powder has to be cut and measured quickly and accurately. The method consists of cutting approximately one-fourth the length of each of three powder grains. The first grain is taken and measured when one-tenth of the block of powder has been pressed through the die; the second grain is taken when one-half the block of powder has been grained, and the third grain when nine-tenths of the powder block has been grained. A microscope having a micrometer stage attachment is used for obtaining the measurements by the same method as previously described for measuring dry powder, and the results should show that the powder has an outside web thickness greater than the inside web thickness. The outer web may exceed the inner web by 15 per cent, but the inner web may not exceed the outer web by 5 per cent. These percentages are calculated on the average web thickness. If these trial measurements do not fulfill the requirements, the dimensions for a new pinplate must be calculated. If the outer web is too heavy it may be made smaller by increasing the diameter of the pin circle. This has the effect actually of increasing the inner web; on the other hand, in the event that the inner web is too heavy, it is necessary to design a new pinplate with a smaller pin circle. With these changes, the calculated shrinkage must be redetermined in accordance

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with the formula given above. The alteration of the die should not include a change of the outside diameter of the die (D), for the reason that such a change would necessitate the use of a new die body. The three dimensions which may be altered as necessity dictates are, the inner web, outer web, and diameter of the perforation.

Failure of powder in ballistic tests.—In the event that the ballistic test shows the lot of powder is too quick or too slow, thus resulting in the failure of the powder ballistically, these circumstances necessitate the recalculation of the die dimensions for the graining of another lot of powder. If the powder is too slow, the average web must be decreased, provided that the outside diameter is not changed. If the powder is too quick, the web average must be increased without altering the diameter. If the powder passes all the ballistic and physical tests, it proves that the design of the die is satisfactory and may be considered as a standard.

Formulæ for burning surfaces.—The calculations of the burning surface of a powder grain are necessary to determine the "quickness" or "slowness" of a powder. The pressure of the gases from the burning powder varies directly as its burning surface. The burning surface was formerly considered the standard dimension by which a satisfactory powder was recognized, but during the last two or three years all powders are gauged by their average web thickness.

The following series of formulæ show how the algebraic expression for the burning surface was derived. It is the product of the number of grains per pound multiplied by the surface of one grain:

A =area of one end of grain.
A' =area of seven holes.
d =diameter of perforation in inches.
D =outside diameter of grain in inches.
L =length of grain in inches.
N =number of grains per pound.
s =surface of one grain.
S =burning surface of one grain.
V =volume of one grain.
W =web thickness or average web.
W_i =web, inner.
W_o =web, outer.
$x = \frac{D}{d}$
$y = \frac{L}{D}$
$\pi = 3.1416 \times \frac{1}{4} = .7854$
δ =specific gravity of powder.

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Formulæ for burning surface—Cylindrical grain—Seven perforations.

1. The formula for the surface of one grain is as follows:

$$\begin{aligned}
&\delta[(D^2\times.7854)-(d^2\times.7854\times7)]+\pi dL7+\pi DL\\
&=(2D^2\times.7854-2d^2\times.7854\times7)+\pi dL7+\pi DL\\
&=\left(2D^2\times\frac{\pi}{4}-2d^2\times\frac{\pi}{4}\times7\right)+[\pi L(D+7d)]\\
&=\frac{\pi}{2}D^2-\frac{\pi}{2}7d^2+\frac{\pi}{2}[2L(D+7d)]\\
&=\frac{\pi}{2}[D^2-7d^2+(2L(D+7d)]\\
&=\text{surface.}
\end{aligned}$$

2. The volume of one grain is equal to the area of the base times the length:

$$\begin{aligned}
&(D^2\times.7854-d^2\times.7854\times7)L\\
&=\left(D^2\times\frac{\pi}{4}-7d^2\times\frac{\pi}{4}\right)L\\
&=\frac{\pi}{4}(D^2-7d^2)L\\
&=\text{volume.}
\end{aligned}$$

3. There are two methods for calculating the number of grains per pound: One by physical measurement described on page 110 and which is performed in the laboratory; the other by calculating from the following formula:

$$\begin{aligned}
&\frac{1.0}{[(D^2\times.7854)-(d^2\times.7854\times7)].0361L\delta}\\
&=\frac{1.0}{\frac{\pi}{4}(D^2-7d^2).0361L\delta}\\
&=\frac{1.0}{(D^2-7d^2).02835294L\delta}\\
&=\text{number of grains per pound.}
\end{aligned}$$

4. The following series show how the formula for burning surface has been found. It is the product of the number of grains per pound and the surface of one grain. It is measured in square inches per pound:

$$\begin{aligned}
&\left(\frac{1.0}{(D^2-7d^2).02835294L\delta}\right)\left(\frac{\pi}{2}[D^2-7d^2+(2L(D+7d))]\right)\\
&=\frac{\frac{\pi}{2}[D^2-7d^2+[2L(D+7d)]]}{(D^2-7d^2).02835294L\delta}\\
&=\frac{D^2-7d^2+[2L(D+7d)]}{(D^2-7d^2).01805L\delta}\\
&=\text{burning surface square inches per pound.}
\end{aligned}$$

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5. In the following formula N is determined by weighing any convenient quantity, counting the grains and calculating from this data the number of grains per pound as follows:

$$\frac{\pi}{2}N[D^2-7d^2+(2L(D+7d))]$$

$$\frac{\pi}{2}=1.5708$$

$$=\text{burning surface square inches per pound.}$$

Formulæ for burning surface—Cylindrical grain—Single perforation.

6. The following formula gives the surface of one grain:

$$2(D^2\times.7854-d^2\times.7854)+\pi dL+\pi DL$$

$$=\left(2D^2\times\frac{\pi}{4}-2d^2\times\frac{\pi}{4}\right)+[\pi L(D+d)]$$

$$=D^2\times\frac{\pi}{2}-d^2\times\frac{\pi}{2}+\frac{\pi}{2}[2L(D+d)]$$

$$=\frac{\pi}{2}[D^2-d^2+2L(D+d)]$$

$$=\frac{\pi}{2}(D-d+2L)\ (D+d)$$

$$=\text{surface.}$$

7. The volume of one grain is equal to the area of the base times the length:

$$(D^2\times.7854-d^2\times.7854)L$$

$$=\left(D^2\times\frac{\pi}{4}-d^2\times\frac{\pi}{4}\right)L$$

$$=\frac{\pi}{4}(D^2-d^2)L$$

$$=\text{volume.}$$

8. The number of grains per pound can be calculated by actual measurement as described on page 110 and it can also be found by the following formula:

$$\frac{1.0}{\frac{\pi}{4}(D^2-d^2).0361L\delta}$$

$$=\frac{1.0}{(D^2-d^2).02835294L\delta}$$

$$=\text{number of grains per pound.}$$

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9. From the above formulæ, the formula for burning surface is found by multiplying the number of grains per pound by the surface of one grain:

$$\frac{\frac{\pi}{2}(D-d+2L)\ (D+d)}{(D^2-d^2).02835294L\delta}$$
$$=\frac{[(D-d)+(2L)]\ (D+d)}{(D^2-d^2).01805L\delta}$$
$$=\text{burning surface square inches per pound.}$$

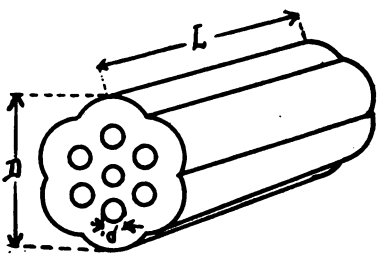
10. In the following formula N is determined by weighing an approximate quantity and counting the grains, calculating from this data the number of grains per pound:

$$\frac{\pi}{2}N(D+d)\ (D-d+2L)=\text{burning surface square inches per pound.}$$

Formulæ for burning surface—Sliverless grain—Seven perforations.

11. There are several methods for calculating the burning surface of the sliverless grain, using different geometrical forms, and the following formula has been calculated from the accompanying geometrical figure, which is a simple problem in geometry:

$$S=\frac{2A+61L+7\pi dL}{AL\times.0361\times\delta}.$$



12. Another formula for the burning surface of sliverless grains is given in the Inspector's Manual as:

$$S=\tfrac{1}{8}N[2\pi(D(4L+D)+14d(2L-d))+3D^2V^2]$$

where N=number of grains per pound.

CONCLUSION.

General considerations.—It has been found that, on the whole, the cylindrical form of grain is most satisfactory; that 100 per cent solvent is the average amount used for regular cannon powder; that air-dried powders give a smaller per cent shrinkage and their dies are therefore easier to calculate.

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In calculating the dies for powder, the average web is taken as a basis and the dimensions are first calculated by formula and then changed as conditions in manufacture require. If a powder is too quick the average web must be increased, and if too slow, decreased.

Records should be made of all powders calculated on cards similar to the following data card:

SMOKELESS POWDER DATA.

Size	Model	Lot No.	W. O
DIE NO.	PIN PLATE NO.	DWG. NO.	REV.

FORM OF GRAIN

	L	D	d	Wo	W	Wa
Dimensions of Die						
% Shrinkage Allowed						
Required Dimensions of Dry Grain						
Measured Dimensions of Dry Grain						
Actual Shrinkage %						

Dia. Pin Circle	Kind of Pins	Slope of Cone

Grained From To

Wt. of Lot Packed

L : D (y)		D : d (x)	
Req:	Actual	Req.	Actual

% Solvent	Ether / Alcohol	No. of Perforations	Gravimetric Density Lbs. per Cu. Ft.	Ref. P. A.

Total Vol. (D. H.) %	Total Vol. (Pkd.) %	Alcohol / Water	Sp. Gr. Assumed / Actual

No. Grains Per Lb. (Finished)		Burning Surface Per Lb. Sq. Ins. (Finished)		Diff. Between Wi and Wo ip % of Wa (Finished)	
Required	Actual	Required	Actual	Required	Actual

CUTTER NO.

FEED ROLL	Dia. Cir.	DRIVING GEARS	No. Teeth DriveR
	Face		No. Teeth DriveN
	Dwg. No.		D. Pitch
BAND WHEEL	Dia. Cir.	FEED PLATE	No. Holes
	Face		Dia. of Holes
	Dwg. No.		Dwg. No.
BAND	No. Teeth	MOTOR	HP
	Bet. Cutting Edges		R. P. M
	Length of Tooth		Dia. Pulley
	Width of Slot	Pulley on Cutter	Dia.
	Thickness	R. P. M. Band Wheel	
	Width	R. P. M. Feed Roll	
	Length	Travel of Band	Ft. Per Min.
FEED ROLL GEARS	No. Teeth	Constant	
	Pitch Dia.		
	D. Pitch		
	Face		

CUTTER NO. (NAVY)

DRIVING GEARS	No. Teeth DriveR	
	No. Teeth DriveN	
	D. Pitch	
Worm		
No. Teeth Worm Gear		
No. Knives		
Feed Rolls	Dia. Bot. Groove	Angle
	HP	
MOTOR	R. P. M	
	Dia. Pulley	
Pulley on Cutter	Dia.	
R. P. M. Knife		

FINISHING PRESS.

PRESS NO.	PRESSURE IN POWDER CYLINDER LBS. PER SQ. IN			VELOCITY OF EXTRUSION	NO. OF DIES	NO. DIE HOLDERS
	Min.	Max	Ave	Feet per Minute		

PLATE 34.

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CHAPTER III.

STABILITY OF SMOKELESS POWDER.

The subject of stability of smokeless powder involves both safety in storage and uniformity in ballistics. In the discussion upon the purification of nitrocellulose, it was pointed out that the processes of boiling are made necessary from the fact that a pure product, or more properly, one definite nitrate, can not be prepared. The present knowledge of the cellulose molecule and of the intermediate reactions occurring during the nitration of the molecule, limits any attempt at the preparation of a single nitrate, and while the complete hydrolysis of the lower nitrates is sought in the boiling processes, there is no assurance that this reaction is the only one concerned, nor is it proven that there are not other factors influencing the speed and the completeness of the reaction. In spite of the elaborate process of purification followed out to insure the stability of the finished powder, this program is extended by incorporating in the colloid four-tenths per cent dry weight of diphenylamine.

STABILITY TESTS.

The powder is said to be stable or is said to have good stability when it passes the KI test, the 135° test, and the test in the two sets of surveillance chambers, one of which is maintained at a temperature of 65.5° C. and the other at 80° C.

There is no test, however, of the stability of smokeless powder which is infallible, or which indicates in more than a general way the safety of the powder from the storage standpoint. The idiosyncrasies and the unreliability of the KI test are too well known to require more than passing mention. The 135° test serves as a criterion for the incomplete hydrolysis of the lower nitrates and for the presence of sulphuric esters (cellulose sylphates). Any of these are capable of giving a low test for "salmon pink." There is a good deal of discussion, however, upon the points involved, and research work projected along physico-chemical lines would throw much needed light upon this subject.

The surveillance tests of smokeless powder are unsatisfactory from the standpoint of uniformity of results and also from the standpoint of elapsed time necessary to obtain any data.

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CAUSES OF INSTABILITY.

Worden points out (Nitrocellulose Industry, Worden, D. Van Nostrands Co., New York, 1911) that the stability of cellulose nitrate may be influenced by any or all of the following factors:

First. The formation during the process of nitration of sulphuric esters, which are not entirely eliminated in the subsequent purification processes.

Second. The presence of hydro- and oxy-cellulose in the cellulose before it is nitrated. This point has already been emphasized in the discussion on nitration, where it was pointed out that the overbleaching of the raw material yielded a product relatively high in soluble cellulose.

Third. Traces of free acid.

Fourth. Traces of organic impurities, such as waxes and resins.

Fifth. The presence of fungi or other microorganisms.

Sixth. The presence of such vaguely characterized bodies as nitrosaccharoses or pectins.

STABILIZERS.

Prior to 1908 little was done from the manufacturing standpoint to standardize the methods of purification then in practice. In fact, the importance of the whole subject of stability of explosives was not recognized to the same extent as at present and consequently had not received the same consideration. In the mixing of the colloid, it was the practice to incorporate a small amount of an organic dye which served the purpose of an indicator rather than a stabilizer.

The indicator which found the widest application was rosaniline, and its adoption was due to the fact that upon the development of any marked acidity produced from the decomposition of the smokeless powder, the red color of the dye in the powder grains faded to a yellow, which fact serves to indicate the instability of the powder.

The use of diphenylamine was not general until the latter part of 1908, and its function was different from that of Rosaniline, for it has the property of combining with free NO_2. Upon the development of those free oxides of nitrogen in smokeless powder, the diphenylamine undergoes progressive nitration (Buisson, " Problems, Des Poudres," P. Juillard, Bul. Soc. Chem. 33, 1905, p. 1172), as indicated in the following series of reactions:

$(C_6H_5)_2NH$	$(C_6H_5)_2N.NO$	$C_6H_4(NO_2).N(NO).C_6H_5$
diphenylamine	diphenyl-nitrosamine	nitro-diphenyl-nitrosamine
$(C_6H_4NO_2)_2NH$		$C_6H_4(NO_2).N.C_6H_3(NO_2)_2$
dinitro-diphenylamine		trinitro-diphenylamine

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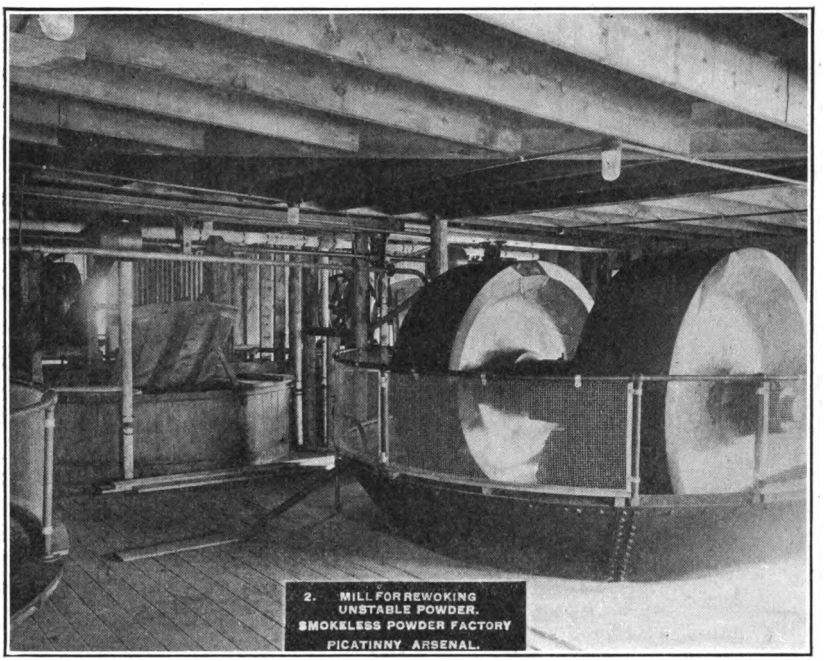

PLATE 35.

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These separate substances may be detected by various quantitative and qualitative reactions, and when any of the tests applied to the powder are positive, they indicate an impaired stability.

REWORKED POWDER.

The reworking of smokeless powder, which is in effect a salvaging of unstable powder, is a relatively new development in the manufacture of this propellant and is, therefore, experimental from many standpoints. The subject of stability of organic nitrates, of which this material is an example, and of organic nitro bodies is one of very prime importance, particularly when large amounts of explosive are being stored. In fact, the whole storage problem is so intimately related to stability that a consideration of the one necessarily involves the other.

When storage tests and surveillance results give warning of an approaching impaired stability of a quantity of smokeless powder, the particular lot so affected is withdrawn from general magazine storage, each powder container opened and the contents flooded with water. In the event that the lot in question is a nitroglycerin powder or a coated powder such as a graphited powder, the lot is destroyed at the burning ground. This procedure is made necessary for the reason that it is impracticable from the standpoints of both economy and safety to rework such powders. If, however, the powder showing impaired stability is a so-called "straight nitrocellulose" powder, the reworking can be accomplished economically and efficiently. It is necessary, however, to determine the nitrogen content in the unstable powder, for a powder whose instability has progressed to such a degree that the loss of nitrogen brings the percentage of the total nitrogen below 12.10 per cent can not be reworked to advantage. A powder failing to show at least this percentage is burned as in the case of the nitroglycerin and coated powders.

The fabrication of reworked powder differs from that of straight powder in that there are no nitrating, boiling tub, or pulping processes involved. Instead of this the powder grains are pulverized under water by a heavy steel wheel mill weighing 5 tons, until the particles of powder are so finely comminuted that they float on the surface of the water. A discharge pipe from the mill conveys the material to a screen having a mesh of twenty-six hundredths of an inch, where the coarser particles of powder are separated out and returned to the mill for further grinding. The grinding operation is therefore of a continuous nature and more old powder is added from time to time, depending upon the hardness of the grains being worked and the speed of the mill.

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After this preliminary screening the material is repurified in a manner similar to that employed in the poaching treatment of the regular pyro. The reworked pyro at this stage is very dissimilar to the regular pyro and presents many obstacles from the manufacturing standpoint. It is yellowish in color, does not respond readily to the purification treatment, is difficult of manipulation in the wringers on account of the dense cake it forms on the screen, and offers many problems in chemical analysis, especially when determining the percentage of nitrogen. In the dehydrating presses the utmost care must be exercised, for on different occasions the careless manipulation of the pressure valves has resulted in the blowing up of the press, with its attendant fire and loss of life. The dehydrated block, unlike the regular pyro, is more friable and is in fact so lacking in cohesiveness that it can not be put in the block-breaker prior to the mixing operation.

Its photomicrograph also shows certain definite differences, one of the most striking being the reduction in the number and size of the fibers, thus indicating the action of the previous colloiding operation. It is largely due to this fact that reworked pyro granulated for 6-inch gun, model 1900, 1903, and 1905, and 75-mm. gun, model 1897, requires only 90 per cent solvent as against 100 per cent in regular pyro.

After the colloid has been formed, however, the treatment in both the factory and dry house does not differ materially from that given the regular colloid.

STORAGE OF SMOKELESS POWDER.

It has already been pointed out that the moisture and volatile content of smokeless powder is an important factor in determining the weight of charge and the pressure to be expected for the required muzzle velocity. In order that this percentage will remain constant it is necessary that the powder be stored in air-tight containers so constructed that they may be easily filled, tested, piled, and emptied. With small arms powder it is customary to line the inside of the container with a muslin bag, the object being to keep the powder entirely free from dust, chips, or other extraneous material.

The powder container consists of a wooden box, zinc lined, about 26 by 16 by 11 inches. There are two types, the so-called export type, having a capacity of 140 pounds of smokeless powder, and the other, the Picatinny Arsenal type, having a capacity of 110 pounds of smokeless powder. The cover is provided with an outside ring, locking ring, and rubber gasket, assembled in such a way that when a lever is forced down on the top of the box, tension is put upon the lugs in such a manner that there is no possibility of air leaks. Each

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box is tested before being filled by having a small hole drilled in the cover, applying compressed air, and noting the reading on the pressure gauge attached to the air line.

The magazines for the storage of smokeless powder should be kept dry, and should be so situated that there is a minimum variation in temperature. This latter point is an important one from the standpoint of maintaining the standard moisture and volatile content. In those instances where a wide range in temperature obtains there is always the added risk of the powder containers tending to develop leaks, due to the difference in the atmospheric pressure inside and outside of the zinc boxes. The most satisfactory storage conditions are those which insure a free circulation of cool, dry air. The ventilation, therefore, of the magazine is a very important point and should be so controlled that air will not be admitted when conditions on the inside of the magazine are such that condensation of moisture within the magazine would follow. The containers should be handled the least possible number times, and whenever such handling is necessary it should be done with the greatest of care, the object being to obviate any possibility of air leaks being produced in the containers.

In piling, the boxes are placed on their broad side. They should not be piled closely together for the reason that such a procedure defeats a proper ventilation. When properly placed, however, they may be piled 12 high, provided the magazine space permits. The important preliminary detail of cleanliness of the magazine floor should not be overlooked, for the accumulation of dirt, rubbish, and nails, aside from being unsightly, constitutes a menace. Scrapers should be placed at the door of the magazine so that mud, cinders, gravel, or other material will be removed from the shoes before the powder is stored. Under ordinary conditions it is not necessary to wear powder shoes in the magazine, except in the case of repacking, when it is advisable that this precaution be observed.

The magazines must be so located that good drainage of the land is possible at all times. This is of special importance where large quantities of smokeless powder are being stored. In spite of the precaution observed for the elimination of leaky powder cans, the fact remains that there are many instances where the leaks are not discovered. This results, of course, in the powder in such cans absorbing moisture from the damp atmosphere in which it is stored, a condition very undesirable from the ballistic standpoint. The fire risk is not of serious consideration if the necessary precautions are observed. The danger of grass fire is practically nil if brush and undergrowth are removed for a distance of 50 feet around the building. The carrying of matches or flash-producing devices of any kind

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should be strictly prohibited. This rule may be enforced by having those employees associated with the storage depot searched for matches in their clothes at irregular intervals. Smoking, of course, should be absolutely forbidden at all times where explosives are manufactured, tested or stored. Oil-burning lamps, lanterns, candles, etc., should be prohibited, and in those cases where artificial light is required special storage-battery lamps should only be used, or for short inspection the ordinary dry battery flashlight.

When it is necessary to renail boxes, nonsparking tools should be used. These consist of copper hammers, wooden mallets, copper nails, etc. The use of metal hooks for the moving of packages of high explosives or ammunition should not be permitted. When circumstances are such that it is impossible to get explosives under cover, a tarpaulin should be thrown over the exposed material, but in the event that an explosive becomes damp from inclement weather, it should be piled separately from the other explosives and a special chemical examination be made of the wet material.

Each magazine should be provided with a minimum and maximum thermometer, and careful record should be kept at all times of the variation in temperature. Except when material is being checked in or out of the magazine, or during inventory, the building should be kept securely locked. Under no circumstances should packages of explosives or ammunition be opened within the magazine. If it is necessary to examine material, it should be done outside of the building and far enough away so that in the event of accident the building itself would not be endangered.

Damaged packages should in every case be removed from the magazine and taken to a special repacking house before any attempt to salvage the material is made. If the damage is slight and a repacking house is not available, any repair or recoopering may be done outside at a distance not less than 100 feet from any magazine.

The transportation of explosives should be governed primarily by the rules of the Interstate Commerce Commission. These provide for the safety in transit of certain so-called acceptable explosives, provided that they comply in every way with the rules for packing and marking. Where shipment is in carload lots, each tier of boxes or containers must be carefully cleated and braced to provide against any possible misplacement through jar or shaking of the car.

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CHAPTER IV.

INSPECTION OF SMOKELESS POWDER.

The foregoing consideration of the manufacture of smokeless powder emphasizes the prime importance of careful chemical supervision throughout the factory and demonstrates that standard methods of analysis are necessary if comparative results from different factories are to be of value. The purchase of the raw materials, such as cotton, acids, alcohol, and diphenylamine, is governed by specifications so designed that a uniform quality of material will be obtained. As these specifications are, necessarily, of a chemical nature, it becomes the function of the laboratories to exercise careful supervision and control over all raw materials purchased.

With this in mind, there has been compiled a set of detailed instructions, based upon methods which have been successfully followed in research and Government control laboratories, as well as in large manufacturing concerns. The raw materials and finished product, therefore, are discussed from the standpoint of adherence to the present specifications in force by the Ordnance Department.

A. Testing of Raw Material.

Both the raw materials used and finished product shall conform to Ordnance Department Specifications 450, dated February 28, 1918, and Ordnance Department Specifications 451, dated August 1, 1918, or subsequent revisions thereof.

METHODS OF ANALYSIS FOR CELLULOSE.

Moisture.—Weigh 5 to 6 grams in a large weighing dish with ground glass stopper. Heat for one and one-half hours at 105° C. Cool in desiccator and weigh. Loss in weight is calculated as moisture on sample taken. Save dried sample for determination of extractive matter.

Extractive matter.—Place (weighed) sample in a Wiley or Soxhlet extractor and add sufficient redistilled ethyl ether for the extracting. Extract on the steam bath for three hours. Transfer the ether to a weighed beaker or glass evaporating dish and evaporate to dryness on steam bath. Heat for 30 minutes in an oven

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at 100° C., cool in desiccator, and weigh. Calculate per cent of extractive matter on weight of dry cotton.

Ash.—Weigh out about 1.5 grams of cellulose in a tared platinum or silica crucible. Moisten with strong nitric acid, then heat gently over Bunsen burner until acid fumes have disappeared, finally heating to a red heat until all carbonaceous matter has been consumed. The crucible should be partly covered with a lid during the heating. Cool in a desiccator and weigh. Calculate the difference in weight as percentage on the dry weight of sample taken.

Test for overbleach.—Boil 5 to 10 grams original sample with distilled water. Filter. Concentrate the filtrate and test portions for chlorides, sulphates, and Ca. Use barium chloride to detect sulphates. Use silver nitrate to detect chlorides (after acidifying slightly with nitric acid).

The material soluble in potassium hydroxide solution will be determined by heating 2 grams of cotton, previously dried at 102–105° C., in a 250 c. c. glass or porcelain beaker with 100 c. c. of the caustic potash solution (10.0±0.1 per cent) for three hours at 100° C., or an equivalent strength of sodium hydroxide solution (7.14±0.1 per cent). Care must be taken to avoid concentration of the solution or undue oxidation of the cotton, due to the exposure of the alkali-soaked cotton to the air. After the heating is completed the cotton and solution are poured into a beaker containing 1 liter of distilled water, the alkali is neutralized with decided excess of acetic acid. The undissolved cotton is then filtered on to a weighed Gooch crucible having an asbestos mat, and thoroughly washed successively with hot water, alcohol, and ether. It is then rapidly dried to constant weight at 102–105° C. The loss in weight is then calculated as per cent.

METHOD OF ANALYSIS FOR DIPHENYLAMINE.

Total diphenylamine.—Bromination in acetic acid solution. From 2 to 3 grams of sample is weighed into a beaker and dissolved in 25 c. c. glacial acetic acid. A solution of bromine in acetic acid (1:2) is then added a drop at a time until a distinct yellow color persists after stirring. The beaker is covered and set aside for 15 minutes at room temperature, during which time a distinct yellow color should remain. The beaker is then placed on a steam bath and heated for five minutes, at the end of which time there should be a yellow color. The beaker is set aside to cool and 150 c. c. water added. The beaker is placed on steam bath and heated till the hand can barely stand the heat and the precipitate is then filtered off and washed five or six times with hot water, and dried to constant weight. The weight of precipitate multiplied by 0.3487, divided by the weight

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of sample, and multiplied by 100 gives per cent of diphenylamine in original sample.

Melting point.—Determine by method described under trinitrotoluene. The capillary tube should be somewhat larger than that used for trinitrotoluene and a thermometer which can be read accurately to 0.5° C. may be used. The melting point should be between 51.5° and 53° C.

Solubility in ether alcohol.—Dissolve 5 to 10 grams in an excess of ether-alcohol mixture (2:1). Filter through tared Gooch crucible. Wash thoroughly with fresh solvent. Dry at 100° C., cool in desiccator, and weigh.

Water soluble.—Boil 10 grams of diphenylamine with 200 c. c. water for one hour in a flask fitted with reflux condenser. Cool to 25° C. and let stand for one hour. Filter into a tared evaporating dish, run to almost dryness on a steam bath. Dry in desiccator over sulphuric acid and weigh.

Aniline.—Stir about 1 gram of sample in 20 c. c. of chlorinated lime solution. This should not acquire a violet color.

Reaction.—Should be neutral or slightly alkaline to litmus paper. Test by method described under trinitrotoluene for acidity.

METHOD OF ANALYSIS OF MIXED ACIDS.

The analysis of mixed acids involves the following operations:

1. Titration with N/10 NaOH for total acidity.
2. Determination of total HNO_3 by nitrometer.
3. Evaporation of HNO_3 and titration of the residue for total H_2SO_4.
4. Titration with N/10 $KMnO_4$ for oxides of nitrogen.
5. Specific gravity.

By calculation the values obtained in the above operations are reported as:

1. Total H_2SO_4.
2. Available HNO_3.
3. Total N_2O_4.
4. H_2O.

The details of the operations and calculation are described below:

1. *Total acidity.*—A sample of approximately 1 gram is run from a Lunge acid pipette into a 500 c. c. beaker containing 150 to 175 c. c. of standard N/10 NaOH. Add 3 to 4 drops of methyl orange indicator and complete the titration with the standard alkali.

Correction for burette reading: For each °C. above the temperature at which the solution was standardized subtract, for each °C. below this temperature add, 0.01 c. c. for each 35 c. c. of NaOH used.

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Calculate the total acidity as per cent H_2SO_4. For this calculation use the formula—

$$\text{Per cent } H_2SO_4 = \frac{n \times f}{S}$$

in which

n=number of c. c. (corrected) of N/10 NaOH used to titrate.

f=factor to convert standard N/10 NaOH to H_2SO_4.

S=weight of sample taken.

2. *Total HNO_3.*—Determine in Du Pont nitrometer. Use a sample of about 2 grams for spent acid, 1⅛ gram for mixed acid, and 0.8 to 0.9 gram for fortifying acid. The nitrometer reading divided by the weight of sample taken multiplied by 4.49807 (Log. 65303) gives: Per cent HNO_3.

3. *Total H_2SO_4.*—Convert total HNO_3 found by the nitrometer to H_2SO_4, by multiplying by 0.77814 (Log. .89106). Subtract this from the total acidity as H_2SO_4. The remainder is total H_2SO_4. As a check on this figure the following determination should be made:

A sample of about 2 grams of mixed acid is run from a Lunge pipette into a large-sized porcelain crucible lid. Place the lid on the small hole of the steam bath and evaporate for one hour with good pressure of steam. Then add 1 c. c. of water, drop by drop, carefully avoiding any spurting. Tilt the lid from side to side to cause a flow of the liquid over the whole surface, and continue the evaporation for one-half hour. Then add another 1 c. c. of water and repeat the operation. This treatment serves to break up the nitrosulphuric acid present, liberating the oxides which evaporate with the water.

Transfer the lid to a 400 c. c. beaker containing 150 to 175 c. c. of N/10 NaOH and titrate exactly as described under total acidity. Calculate the acidity as H_2SO_4 by the formula given above.

4. *Oxides of nitrogen.*—Put about 200 c. c. of distilled water in a 400-c. c. beaker and color it slightly with a small drop of N/5 $KMnO_4$. Then run into the water from a Lunge pipette about 10 grams of acid, using a short piece of glass tubing connected to the tip of the pipette by a very short piece of rubber tubing and dipping below the surface of the water. When the sample has been added the additional tubing should be disconnected and dropped into the beaker. Titrate with N/5 $KMnO_4$ until a pink color persists for 10 minutes. The bulk of the $KMnO_4$ solution may be added at once and then make gradual additions as the color fades. A point will finally be reached when the color fades very rapidly, having just before this time persisted for several minutes with the addition of 1 or 2 drops of solution. Beyond this point about one-tenth of the total amount used is required to complete the titration. It is unnecessary

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to make corrections for slight errors in the burette readings or for temperature, as a considerable error is necessary to affect results.

Calculate the percentage of N_2O_4 from the volume of $KMnO_4$ used and convert it to its equivalent in HNO_3. Subtract this equivalent in HNO_3 from the total HNO_3 obtained in 3. The difference is actual HNO_3.

The actual HNO_3 plus one-half the N_2O_4 calculated as HNO_3 is available HNO_3.

Formula for calculations:

$$\text{Per cent } N_2O_4 = \frac{n \times f}{S}$$

in which

n = number of c. c. of N/5 $KMnO_4$ used to titrate.
f = factor for converting to N_2O_4.
S=weight of sample taken.

To convert N_2O_4 to its equivalent in HNO_3 multiply by 1.36966 (Log. .13661).

5. *Water.*—This is calculated by difference. The sum of the percentages of H_2SO_4, HNO_3, and N_2O_4 substracted from 100 per cent is taken as water.

Standardization of solutions.—NaOH: This is made approximately tenth normal. A large carboy is filled with distilled water which has previously been boiled to remove CO_2 and cooled in running water. Dissolve in a portion of the water 4 grams of NaOH for each liter of water used, filter quickly through glass wool if necessary, avoiding much exposure to air. When the solution is comparatively cool, add it to the water in the carboy, washing out the beaker with a portion of water taken out of the carboy before the soda was added. Mix the solution by blowing air through it which has been freed from CO_2 by passing it through a wash bottle of strong caustic solution. The mixing should be continued for about two hours. If the container is not too large, it may be mixed by shaking by hand. When thoroughly mixed, set the container in its place and connect with a wash bottle containing strong NaOH solution to protect it from the CO_2 of the air.

The solution so prepared should be standardized carefully at least once a week against N/10 H_2SO_4 and HCl. A standard H_2SO_4 of about 90 per cent strength should be kept in a double-sealed bottle in a desiccator and the standard alkali titrated once a month against a weighed sample of this acid.

The values for the standard acid solutions should be based on gravimetric results. The standard N/10 H_2SO_4 and HCl should be standardized at least once a month by the following methods:

For N/10 H_2SO_4: Standardize at 25° C. or make corrections of 0.01 c. c. per °C. for each 35 c. c. above or below 25° C. Make dupli-

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cate determinations, using 50 c. c. for each determination. Dilute to 200 c. c. Add a few drops of dilute HCl. Heat to boiling. Add slowly with stirring 7 to 8 c. c. of 10 per cent $BaCl_2$ solution. Continue boiling a few minutes. Set on steam bath until the precipitate becomes granular and settles to the bottom, leaving a clear solution. Filter while hot through a Gooch crucible containing a mat of acid-treated and ignited asbestos. Wash well with hot water, dry, and ignite for one-half hour at a good red heat. Cool in desiccator and weigh. Calculate the weight of the precipitate of $BaSO_4$ to H_2SO_4 per liter of solution. Find the normality factor of the solution by dividing this weight by 49,045 and express the result to 4 places of decimals.

For N/10 HCl: Standardize at 25° C. or make corrections as for H_2SO_4. Make duplicate determinations, using 30 c. c. for each determination. Add 20 c. c. of water and a few drops of HNO_3. Then add, drop by drop, 6 c. c. of a fresh 10 per cent A_gNO_3 solution with constant stirring. After precipitation is complete wash down the sides of the beaker with a thin stream of water from a wash bottle. Heat to about 70° C., stirring constantly, then set away in a dark place over night. On the following day filter through a white-ribbon S. & S. filter paper and wash with warm water slightly acidified with HNO_3 until all trace of A_gNO_3 is removed. Dry at 100° C., transfer the precipitate to a glazed paper and ignite the filter paper in a weighed porcelain crucible. After carbon has been burned off, add a drop or two of HNO_3 and HCl. Evaporate to dryness, transfer precipitate to crucible and heat to incipient fusion, cool in desiccator and weigh. Calculate the weight of A_gCl to HCl per liter of solution. Find the normality factor of the solution by dividing this weight by 36.47 and express the result to 4 places of decimals.

If it is desired, a Gooch crucible with an asbestos mat may be substituted for the filter paper if the mat is thick and compact and the operator can check results by this method with those by the method described above.

ALCOHOL.

Test for aldehyde.—Prepare the following solutions:

(*a*) Weigh accurately 9 grams silver nitrate, c. p., and dissolve it in 100 c. c. of water.

(*b*) Weigh 9 grams of sodium hydroxide and dissolve it in 100 c. c. of water.

(*c*) A solution of ammonium hydroxide, specific gravity 0.90.

These three solutions should be kept in separate bottles (*a*) in a dark place. For the test put 1 c. c. of silver nitrate solution in a small graduate, add 1 c. c. of sodium hydroxide solution and then 1 c. c. of ammonium hydroxide solution, or until the precipitate is

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just dissolved. Then put 10 c. c. of the alcohol to be tested in a clear glass-stoppered bottle, add 10 c. c. of distilled water and 1 c. c. of the mixture prepared in the small graduate. Shake and allow to stand for one hour in a dark place. Then filter and test the clear filtrate for unreduced silver, by adding a solution of sodium chloride. If silver chloride is precipitated the alcohol contains less than the maximum allowable amount of aldehyde.

The specific gravity is determined by means of a Westphal balance.

Acidity.—Measure 50 c. c. of alcohol into an Erlenmeyer flask, add 3 to 4 drops phenolphthalein as an indicator and titrate with N/100 KOH solution. Calculate acidity as acetic acid.

Formula: $$\text{Per cent acidity} = \frac{\text{c.c. KOH} \times 0.006 \times 100}{50 \times \text{specific gravity.}}$$

The acidity should not exceed 0.01 per cent.

ETHER.

Specific gravity.—Determine specific gravity by the Westphal balance.

Acidity.—Measure 50 c. c. of alcohol into an Erlenmeyer flask, add three drops phenolphthalein solution and titrate to faint pink with N/100 KOH. Then add 50 c. c. of ether and titrate again to faint pink. Calculate acidity as acetic acid by the formula:

$$\text{Per cent acidity} = \frac{\text{c.c. KOH} \times 0.006 \times 100}{50 \times \text{gravity.}}$$

DU PONT NITROMETER.

Theoretical.—The Du Point nitrometer is a modification of the Lunge nitrometer and is devised to avoid the necessity of making the usual correction for temperature and barometric pressure which must be calculated with every gas measurement. The principle of the apparatus is to inclose a known volume of air at such a pressure that it takes up exactly the volume which it would occupy at 20° C. and 760 mm. pressure. If the same pressure and temperature are then applied to another volume of gas this will also take up the volume which it would occupy at 20° C. and 760 mm. pressure. The volume of air is kept in a "compensating tube" which is in connection with the reading tube of the nitrometer. When it is desired to read the volume of a given quantity of NO gas at 20° C. and 760 mm. pressure, the level of the mercury in the "compensating tube" is brought to the mark at which the air within the tube occupies the space it would occupy at 20° C. and 760 mm. pressure, the level of the mercury in the reading tube is brought on a level with this same mark and the reading made. The reading tube on the Du Pont

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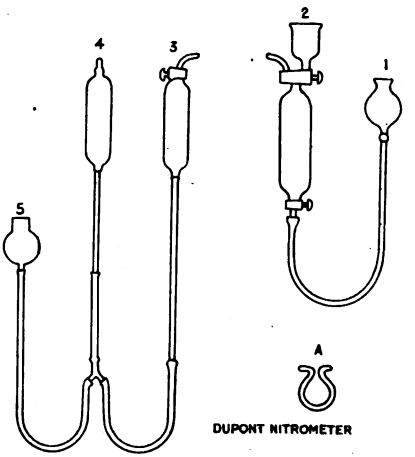
nitrometer is graduated to read directly to per cent of nitrogen when a 1 gram sample is used.

To set up a Du Pont nitrometer.—The various tubes are arranged on the nitrometer rack in order shown in the accompanying sketch; 25 c. c. of 95 to 96 per cent H_2SO_4 are then placed in No. 2 and a quantity of air drawn in through the stopcock. The stopcock is then closed and the bulk shaken vigorously to dry the air. The shaking is repeated several times at intervals of from 10 to 15 minutes. When the air is judged to be thoroughly dry, 2 and 4 are connected and the dry air run into 4 until, with the stopcock of 3 open and the mercury in 3, 4, and 5, on the same level, the reading in 3 is about 12.50. No. 4 is then sealed with a small blowpipe flame. Another portion of air is then desiccated in 2 and transferred to 3 until, with the mercury in 3, 4, and 5 on the same level, the reading in 3 is about 12.50. It is not necessary that these gas volumes be exact or equal. The small manometer, A, is then filled with H_2SO_4 and attached to 3. The apparatus is then left to come to constant temperature. The mercury in 3, 4, and 5 is then adjusted so that the air in 3 is under atmospheric pressure as shown by the acid in A. The reading is taken on the graduated scale on 3. The temperature and barometric pressure are noted at the same time. From these readings the volume of air in 3 is calculated at 20° C. and 760 mm. pressure by the gas laws which are expressed by the equation:



DUPONT NITROMETER

$$V:V'=P':P$$
$$V:V'=T:T'$$

in which

V=volume at 20° C. and 760 mm.
V′=volume at the observed temperature T′ and pressure P′.

From these is derived the equation:

$$V=V'\frac{p'\times 293}{760\times(273+T')}\times\frac{1-(0.00018t')}{1-(0.00018\times 20)}$$

The last term of the equation represents the correction to be applied for the coefficient of expansion of mercury in the barometer where t′ equals temperature of the barometer. When V has been calculated, the mercury in 3, 4, and 5 is adjusted so that, with the

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mercury in 3 and 4 on a level, the mercury in 3 marks the calculated volume of air. The height of the mercury in 4 is then marked by a strip of paper pasted on the tube. This is taken as the standard volume with which every volume of gas to be measured is compared.

Standarization with C. P. KNO_3.—Take a sample of C. P. KNO_3 which has been recrystalized three times from alcohol, grind it fine and dry for one and one-half to three hours at 150° C. Then weigh out in a small weighing bottle exactly 1 gram and transfer it to the nitrometer (for details see "Determination of nitrogen"), dissolving the KNO_3 in the nitrometer cup with 20 c. c. 95 per cent plus or minus 0.3 per cent H_2SO_4. With the lower stopcock of the generating bulb open and the mercury bulb low enough to give a reduced pressure in 2, gently shake the generating bulb until the larger portion of gas has been generated. Then raise 2 until the mercury drops nearly to the lower shoulder, close the lower stopcock and shake vigorously for three minutes. Replace on the rack, open the lower cock, and let stand for several minutes. Then repeat the shaking for an additional three minutes, adjusting the mercury as before. Finally transfer the gas to 3, adjust 3, 4, and 5 so that the level of mercury in 3 and 4 is about on the level and allow to stand 20 minutes. Then carefully adjust the mercury levels with leveling device and take the reading in 3. This should be 13.85 per cent.

Standardization by a test blend.—This standardization is run in a way similar to the above except that a blend of nitrocellulose which has been carefully tested on a standardized nitrometer is used. This method is somewhat more convenient than the method with KNO_3 because the nitrocellulose is more easily broken up in the nitrometer than KNO_3. Whenever a doubt exists, however, the standardization must be carried out with KNO_3.

B. Testing of Nitrocellulose.

Ether-alcohol-insoluble material.—The percentage of ether-alcohol-insoluble material in nitrocellulose may be determined as follows: Soak 1 gram of the dry sample for two hours in 50 c. c. of 95 per cent alcohol in an Erlenmeyer flask. Then add 100 c. c. of ethyl ether, shake and allow to stand overnight. On the following morning the mixture is shaken thoroughly and transferred with washing by 80–100 c. c. of fresh ether-alcohol mixture (2:1) to a specially constructed solubility tube of the following dimensions: Total length, 21 inches; inside diameter, 1.35 inches; the lower end constricted for a distance of 2 inches to an inside diameter of 0.3 inch and graduated in one-tenth c. c. to 10 c. c. The constricted portion should be tapered gradually from the large part of the tube and the graduations should extend to the top of the shoulder thus formed. After standing for seven hours in the solubility tube

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the volume occupied by the insoluble and semisoluble matter is read in c. c. from the scale on the tube. This number (of c. c.) multiplied by 0.5 is the percentage of ether-alcohol-insoluble matter as noted in the specifications for smokeless powder.

The official temperature for this determination shall be 15.5° C. and in case of doubt or for greater accuracy the complete determinations shall be made at this temperature, the solvents being brought to this temperature before their addition to the sample. The insoluble material should not exceed 5 per cent. If it exceeds 5 per cent (10 c. c.) this method must be discarded and special quantitative methods devised.

Heat test 65.5° C. with potassium-iodide starch paper.—The sample shall be pressed in a clean cloth or wrung in a wringer if it contains a large excess of water. The cake shall be rubbed up in a cloth until fine, taking care that it does not come in contact with the hands, spread out on clean paper trays and dried in an air bath at 35° to 43° C. just a sufficient length of time to reduce the moisture to that amount which will give a minimum heat test, this amount being from 1.5 to 2 per cent.

During this time the tray is taken out several times and the nitrocellulose is "rubbed up" with a piece of tissue paper spread over the back of the fingers. When the nitrocellulose begins to stick to the tissue paper, due to static electricity which is developed when dry nitrocellulose is rubbed, take a sample of 1.3 grams and put in KI starch test tube, shaking it down to occupy about 1⅝ inches in the tube. These tubes for this test are standard 5½ inches long, one-half inch internal diameter, and five-eighths inch external diameter, closed by a clean cork stopper fitting tightly, through which passes a tight fitting glass rod with platinum holder for the paper. Continue the drying and rubbing, taking samples at appropriate intervals of two to five minutes until the sample on the tray is completely dry and five samples have been collected. This series of samples is called the "moisture series" and is taken in order that samples may be run containing varying percentages of moisture.

If, as sometimes happens in dry weather, the moisture has been reduced to less than 1.5 per cent, the sample shall be placed in a moist atmosphere for a time not exceeding two hours until the required moisture percentage is obtained. The whole time of drying and making the test shall not exceed eight hours.

When these five samples have been collected they are prepared for the test as follows: Select a clean, fresh cork stopper which just fits the tube. Perforate it and introduce a short length of closed glass tube into the lower end of which a small piece of platinum wire has been fused. Burn off the platinum wire in a flame. Then fix on it a strip of KI starch paper 1 inch in length, three-eighths inch wide.

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This should not be touched with the fingers. Draw across the paper near its upper end a glass rod which has been dipped into a solution composed of one part glycerine and one part distilled water. Then fit the stoppers so prepared into the test tubes containing the samples to be tested. Immerse the five tubes in the specially prepared heating bath, which is kept at a temperature of 65.5° C. ± 1° C. Then note carefully the appearance of the first faint yellow line at the lower edge of the moistened portion of the test paper. This discoloration is to be greater than that obtained at the same time by a blank test. The tube giving this color first is taken as the test for the lot. This time shall be not less than 35 minutes.

Standard test papers will be used and will be furnished by the department to manufacturers.

The standard water bath holds 10 tubes and is made long and narrow to reduce to a minimum the upper portions of the tubes. These tubes are immersed in the bath to a standard depth of 2.25 inches.

Test at 135° C.—A sample of nitrocellulose is laid out in paper trays and dried for four or five hours at 42° C., or is dried overnight at room temperature and then further dried one-half hour at 42° C., after which 2.5 grams are pressed into the lower 2 inches of each of two tubes of heavy glass, about 290 mm. long, 18 mm. outside diameter, and 15 mm. inside diameter, closed with a cork stopper through which a hole 4 mm. in diameter has been bored. A piece of standard normal methyl violet paper, 70 mm. long and 200 mm. wide, is placed in each tube, its lower edge 25 mm. above the cotton. When the constant temperature bath has been carefully regulated at 134.5° C., plus or minus 0.5 C., these tubes are placed in the bath so that not more than 6 or 7 mm. of length projects from bath. Examination of the tube is made each five minutes after 20 minutes have elapsed by withdrawing about one-half its length and replacing quickly. When salmon pink is obtained between examinations, after 25 minutes and before 30 minutes, a 30-minute record shall be allowed the sample. The methyl violet test paper in either tube shall not be completely turned to standard salmon pink in less than 30 minutes.

The test is continued for five hours and no explosion should occur in that time.

The bath must be placed in a good light with a suitable background.

There shall be no failure of either of the tubes.

The standard normal methyl violet papers will be furnished by the department.

Determination of nitrogen.—A sample of approximately 1 gram is taken. This is weighed in a small weighing bottle, dried one and one-half hours at 100° C., cooled in a desiccator, reweighed and

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transfered to the cup of the nitrometer. Measure out 20 c. c. of 95 per cent plus or minus 0.3 per cent H_2SO_4. Pour a portion of it into the cup and wash the nitrocellulose into the generating bulb. Rinse out the weighing bottle with successive portions of acid, pouring into the nitrometer cup each time and running into the bulb. If the nitrocellulose is very dusty, it is best to dissolve it in the weighing bottle before transferring. Each successive portion of acid poured into the cup should be directed by means of a small stirring rod so that it rinses down the sides of the cup. When all is in the bulb, the NO gas is generated just as described under standardization. The gas is transferred to the measuring tube and the reading taken after standing 10 or 15 minutes. The reading is corrected for the sample, above or below 1 gram, the result being the percentage of nitrogen in the sample. If exactly 1 gram of sample is employed no correction is necessary.

Ash.—Weigh approximately 1 gram of sample in a tared crucible. Moisten with a small quantity of concentrated nitric acid and digest for two or three hours on the steam bath. Then place on a triangle and heat with a Bunsen burner, very cautiously at first to avoid loss. Finally place crucible in an inclined position, partly cover with lid and heat strongly over the blue flame of a Bunsen burner until all carbonaceous matter has disappeared. Cool in desiccator and weigh.

Acetone insoluble material.—This (heretofore-called "organic residue") is obtained by dissolving 1 gram of nitrocellulose in 100 c. c. of pure acetone in an Erlenmeyer flask and then transferring to a "solubility tube" which is described in paragraph headed "Ether-alcohol-insoluble material" and continuing as prescribed in that paragraph.

C. Testing of Smokeless Powder.

Ten normal grains will be taken and both ends cut off at right angles to the length until—

$$\frac{\text{diameter}}{\text{length}}=1.$$

These pieces are accurately measured for length and then slowly compressed between parallel surfaces until the first crack appears. The pressure is then removed and the grain again measured. The decrease in length necessary to crack the grain is calculated to per cent of original length. The average compression must not be below 35 per cent. In case of failure in this test 20 more grains are tested, and if the average compression of the total 30 grains is below 35 per cent the powder will be rejected. Grains accidentally abnormal in shape or containing obvious flaws will not be used for this test.

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Gravimetric density.—Weigh accurately the amount of powder required to fill box exactly 1 foot in every dimension, inside measurements. Report as pounds and decimal fraction of pounds.

Specific gravity.—For 3-inch field gun and smaller calibers, determine by the following method: Place an accurately weighed sample of 15 to 20 grams, using whole grains, in a standardized specific gravity bottle. Cover with boiled distilled water and hold under a vacuum not less than 500 mm. until all air is displaced or approximately 20 minutes. Fill the bottle with boiled distilled water at 15.5° C. and weigh. Subtract the weight of the bottle plus powder. This gives the weight of water in the bottle. The difference between this weight and the weight of water in the bottle when it was first weighed with the sample of powder represents the weight of water displaced by the powder.

Measurements.—Thirty grains will be selected at random and measured for length, diameter, perforation, and (inner and outer thickness) webs.

For grains having seven perforations the outside diameter (D) of the grain shall be about 10 times the diameter (d) of the perforations, and the length (L) from 2.1 to 2.5 times the outside diameter. For grains having a single perforation the outside diameter (D) shall be about three times the diameter (d) of the perforation, and the length (L) about three times the outside diameter. The dimensions (L and D) of at least 30 grains specified must comply with the requirements for uniformity as per table.

Dimensions.	Mean variation of individual dimensions from mean dimensions, expressed in per cent of mean dimensions.	
	Permitted.	Desired less than—
L.....	5.0	1.0
D.....	2.5	0 5

For grains having seven perforations six measurements of the outside-web thickness (Wo) and of the inside-web thickness (Wi) will be made from the six outside holes for each of the 30 grains, and the two sets of 180 measurements will be averaged to obtain the mean outside and inside webs. The powder shall have the inside-web thickness as nearly as practicable about 5 per cent less than the outside-web thickness. The outside-web thickness may exceed the inside-web thickness by 15 per cent and may be less than the inside-web thickness by 5 per cent. The percentages are calculated on the average web thickness.

For grains having a single perforation take the greatest and least web measurements of each of the 30 grains. Neither the average of

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the 30 least measurements nor the average of the 30 greatest measurements should differ more than 15 per cent from the average of the entire 60 measurements, which is the average web of the powder.

Approximately one-third the length of each powder grain is cut from each end of 30 grains. The remaining one-third of the grain or middle portion of the original grain is "faced" and the end surfaces made exactly parallel. Care must be taken to have clean perforations and edges. A microscope having a micrometer stage attachment is used for obtaining the measurements.

The grains are measured three times across for seven-perforation powder and once across for single-perforation grains.

The number of measurements taken on seven-perforated powder are therefore as follows:

Three measurements of diameter (D); six measurements of outside-web thickness (Wo); six measurements of inside-web thickness (Wi); three measurements of the center hole are taken on each of the 30 grains and six measurements of other perforations on the same number of grains.

Grains per pound.—This should be very accurately determined by weighing an appropriate quantity and counting the grains, calculating from this data the number of grains per pound. If the weight is taken in grams, calculate the number of grains per kilogram and divide by the factor 2.20462. This gives grains per pound. For .30 caliber powder, weigh 2 grams. For other sizes of powder up to 4.7-inch howitzer, weigh 1 pound. All counts should be made in duplicate samples. The average of the two is reported.

Burning surface.—Use the following formula in which—

D=diameter of the grain in inches.
d=diameter of perforation in inches.
L=length of grain in inches.
N=number of grains per pound.

Formula for powder containing seven perforations:

$$\text{Burning surface}=\tfrac{1}{2}\pi N[D^2-7d^2+2L(D7d)]$$

Formula for powder containing one perforation:

$$\text{Burning surface}=\tfrac{1}{2}\pi N(D+d)(D-d+2L)$$

Formula for sliverless grains:

$$\text{Burning surface}=N[2[(A-7A_1)6A_2]+61L+2\pi dL]$$

A=area of hexagon drawn from reentrant angles.
A_1=area of perforation.
r=radius of circle drawn from center of outside perforation and 1 the arc.
1=.0175×r×E.
E=included angle of arc.

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Determination of moisture and volatiles.—Select at least 10 grains and chip several thin shavings from each grain, discarding the end portion. If the powder is too small to chip conveniently, whole grains may be used. The chipping should be done as rapidly as possible and chips dropped quickly into a weighing bottle to avoid loss of volatiles from the freshly cut surfaces. Quickly weigh approximately 1 gram of these chips into a low form 250 c. c. "volatile beaker" which has been thoroughly cleaned, desiccated, and weighed. Use this weight of beaker in final calculations. Add 50 c. c. of redistilled alcohol and 100 c. c. of redistilled ether. Place beaker under a tight bell jar until solution is complete. This usually requires one to two days. The mixture should be stirred occasionally to hasten solution. More ether should be added if much of the ether has been evaporated and solution is not yet complete. Residue determinations should be made on ether, alcohol, and water used in the process and corrections applied to the final weight of the precipitate.

When all lumps have disappeared, place the beaker on the steam bath and evaporate off a portion of the ether. The amount of ether that is evaporated here is very important, since it determines the nature of the nitrocellulose which is precipitated in the next step. If too little is evaporated, a fine sandy precipitate is obtained and the contents of the beaker are likely to "bump" in drying. If too much is evaporated, a gummy precipitate is obtained which can not be dried completely. A gummy precipitate should be avoided. A fine flaky precipitate will give the best results. The amount to be evaporated can be learned only by practice. Approximately 1½ to 2 inches of solution should be in the beaker when the nitrocellulose is precipitated.

When the proper point is reached, take the beaker off of the steam bath and add 50 c. c. of distilled water which precipitates the nitrocellulose. A precipitate of the proper mixture may be obtained in determination by adhering closely to the following procedure: While still warm add, with stirring, 5 c. c. of distilled water from a graduate containing 50 c. c. Stir until precipitate has been disintegrated. Add about 5 c. c. more and repeat above operation. If the precipitate appears to be thick and heavy, add, with stirring, about 5 c. c. of ether at a time until precipitate becomes light and flaky. Then add slowly, with constant stirring, the remainder of 50 c. c. of water.

After precipitation is complete the beaker is replaced on the steam bath and stirred carefully until the bulk of the ether has been evaporated and there is no longer danger of "bumping." In stirring avoid touching the sides and bottoms of the beaker as much as possible. When there is no longer signs of foaming, the

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beaker is suspended in the bath by means of specially constructed wooden blocks and allowed to evaporate to dryness. Do not allow to remain on bath any longer than is actually necessary for drying. On removal from the bath the precipitate should be white or grayish white. A yellow or greenish yellow color indicates that the precipitate has been on the bath too long. Then wipe the outside of the beaker clean and put it in an oven at 100° C. quickly. Before the desiccator is opened, adjust weights on the scale pan to balance the beaker as nearly as possible. If more than 10 seconds are required to get the weight of the beaker, it will have absorbed enough moisture from the air to seriously affect the results and should be put back in the 100° C. bath for 30 minutes more and the weighing repeated. This second check weighing is advisable in all cases where accurate work is important.

The difference between the weight of the sample taken and the weight of the precipitated nitrocellulose is calculated as moisture and volatiles. Deduct 0.01 per cent from this result to allow for the volatilization of diphenylamine in the powder. If the powder contains more or less than 0.4 per cent of diphenylamine, make the proper correction, assuming that 25 per cent of the diphenylamine volatilizes.

Diphenylamine in smokeless powder.—Put 5 grams of powder in a 250 c. c. beaker. Pour 30 c. c. of concentrated HNO_3 over it. Cover with a watch glass and set on steam bath until the powder is completely dissolved. Continue the heating for one-half to one hour after solution has taken place to insure complete decomposition of the nitrocellulose. Then cool and pour into another beaker containing about 100 c. c. of cold distilled water, stirring constantly during addition. Wash out the beaker and watch glass into second beaker, stir vigorously, and set on the steam bath until the precipitate collects in a flocculent form and the solution is a clear yellow color. Cool, filter through a weighed Gooch, dry at 100° C., and weigh. Extract with acetone. Dry and weigh again. The loss equals the nitrodiphenylamine formed. Multiply by the factor 0.40576 to convert to diphenylamine.

This method is much more rapid than the bromination method and gives good results, which are somewhat higher than the latter method.

Determination of alcohol in powder.—Weigh 100 grams sliced powder (unnecessary to slice 3-inch or smaller) into 1,000 c. c. distillation flask. Connect with a condenser and cork the neck tightly with a rubber stopper that has a wide-mouthed separatory funnel through it. Add 25 to 50 c. c. H_2O and 25 c. c. NaOH (30 to 40 per cent) and warm gently. At this stage great caution is necessary. When vio-

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lent decomposition has ceased, add NaOH from time to time until total decomposition of powder has been effected. When this stage is reached, increase the heat and distill off 150 to 175 c. c. of liquid, replacing with H_2O lost from time to time by distillation.

The distillate is neutralized or made slightly acid with H_2SO_4 and 100 c. c. redistilled. Bring to 20° C. and read the refractine index at 20° C. with Zeiss immersion refractometer. From the Zeiss reading the amount of alcohol may be found by reference to tables.

Test at 135° C.—This test is run on all powders. Duplicate tests should be made. Large mixed grains are turned down on a lathe until they fit snugly into the regular 135° test tube.

The test will be made on five samples in exactly the same way as for nitrocellulose, the powder being as nearly in whole grains as is consistent with the standard weight of 2.5 grams. No sample shall turn the normal methyl violet paper to standard salmon pink in less than one hour, nor shall any sample explode in less than five hours. Examination of the tubes is made every five minutes. When the salmon pink is established between the observations at the end of 35 minutes and at the end of 60 minutes, a 60-minute test shall be allowed. The end point is established at the end of the five-minute period during which the salmon-pink color develops in the normal methyl violet paper.

Moisture.—To obtain the amount of moisture in water-dried powders, a sample of at least 5 whole grains of not less than 20 grams will be dried for six hours at 100° C.±2° C. at atmospheric pressure, cooled in a desiccator, and the resultant loss of weight determined by weighing. This loss will be considered as moisture, and the difference between this figure and that of the total volatiles by precipitation will be considered as residual solvent.

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CHAPTER V.

COMPOUND PROPELLANTS.

So far there has been considered only the so-called "straight nitrocellulose" powders, that is, those powders which do not contain either inorganic nitrates or high explosives. The propellants yet to be considered are those which are mixtures of nitrocellulose and nitroglycerin, nitrocellulose, and inorganic nitrates, such as barium nitrate and potassium nitrate, and mixtures of charcoal, sulphur, and potassium nitrate.

SPORTING BALLISTITE AND INFALLIBLE POWDER.

This explosive is used primarily as a propelling charge for shotgun and Stokes trench mortar. Instead of being in the form of a cylinder, as is the case with .30-caliber rifle powder or cannon powder, it is cut in the form of square flakes or discs of approximately 0.005 inches in thickness.

The manufacture of sporting ballistite is concerned chiefly with the proper solution and incorporation of soluble nitrocellulose in nitroglycerin in the proportion of 60 per cent of the former to 40 per cent of the latter. By mixing the soluble nitrocotton and nitroglycerin in hot water a partial colloid is formed which is similar in certain respects to the colloid obtained when nitrocellulose is dissolved in an ether-alcohol mixture. The water is then expressed from the mass by passing the colloid under rollers which are heated to about 40° C. This rolling operation is repeated until a uniform mixture of nitrocotton and nitroglycerin is obtained. It is finally cut into square flakes, then coated and blended in the usual manner.

The inspection of ballistite consists only of stability tests:

(*a*) The finished powder shall give a potassium iodide starch paper test of 15 minutes at 82.2° C.

(*b*) 120° C. fume test: A sample of the powder which has been dried at ordinary laboratory temperature overnight shall be used for this test. There is placed in each of two tubes of heavy glass, which are about 290 mm. in length, 18 mm. outside diameter, and 15 mm. inside diameter, 2.5 grams of the material. When the constant temperature bath has been regulated at 120° C., these tubes are placed in the bath so that not more than 6 or 7 mm. of the tubes project from the bath. Examination of the tubes is made by withdrawing about one-half their length and replacing quickly every 5 minutes. The test shall

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be complete when the fumes fill the tubes. The powder shall give a fume test of not less than 15 minutes at 120° C.

The storage of ballistite powder is maintained under the same conditions as nitrocellulose smokeless powder.

E. C. POWDER.

This propellant is generally used for the loading of blank cartridges and consists of colloided nitrocellulose granulated with inorganic nitrates. The main point observed in manufacture is the proper incorporation and mixing of all ingredients. This process is usually conducted by means of a wheel mill in a manner somewhat similar to that used for black powder and reworked powder. Nitrocellulose of approximately 12.9 per cent nitrogen is mixed with about 10 per cent of a mixture of potassium nitrate and barium nitrate, together with a small amount of diphenylamine and a pink coloring matter, and the product granulated by a mixture of water and a suitable solvent, in such manner that it forms small rounded grains. The nitrocellulose in these grains is only partially colloided, acting as a binding material and hardening the surface of the grains.

INSPECTION.

Granulation.—About 95 per cent shall stay on a 40-mesh screen, and not more than 2 per cent shall pass a 60-mesh screen. The powder shall be stable to the following heat tests:

(*a*) K. I. starch paper test: A weight of 1.3 grams shall be taken and tested in the same way as .30-caliber powder. It shall give a test of not less than 35 minutes.

(*b*) Heat test at 135° C.: A weight of 2.5 grams shall be taken and tested in the same way as .30-caliber powder. It shall not turn normal methyl violet paper salmon pink in less than 25 minutes, nor explode in less than 4 hours.

The remaining nitroglycerin and nitrocellulose powders, used for military purposes; namely, pistol and revolver powders, bull's-ey powder, military rifle Nos. 22 and 34, improved military rifle Nos. 17, 23, and 25 will not be discussed in this paper, inasmuch as the processes of manufacture can not be described without disclosing information regarded by the manufacturers as confidential.

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CHAPTER VI.

BLACK POWDER.

GENERAL.

European history contains references to black powder as early as 1250 A. D. Roger Bacon in 1264 performed the first recorded experiments with this material and shortly after this time it was introduced as a propelling charge for the fourteenth century bombard. Authorities differ upon the subject of the origin of black powder. It has been attributed severally to the Chinese, Arabs, and Hindus. It is certain that the alchemists of mediaeval days were familiar, to a certain extent, with the properties of the mixture of saltpeter, sulphur, and charcoal. Certain authorities regard Berchtold Schwarz as the inventor. To him, at any rate, belongs the credit of being the first (1313 A. D.) recorded user of this material in the propelling of stones from a gun. Powder was first used in a meal state. Later camphor was added to prevent crumbling. Graining or granulating is first recorded in 1425, resulting in a stronger and more uniform powder. Classification of the grains by screening is reported by the French in 1525. Black powder gradually replaced all other devices as a propellant, until 1870 it was practically the only propellant used. Its present military use is practically confined to the following:

First. Ignition charges.

Second. Base charge or expelling charge for shrapnel shell.

Third. Manufacture of primers and fuzes.

Fourth. Saluting and blank-fire charges.

Fifth. For time-train rings and combination fuzes.

Sixth. For mixtures with other kinds of propellant powders for use in small arms ammunition.

It is thus seen that in its former function as a propellant black powder has been superseded almost entirely, having been replaced by smokeless powder. Among some of the factors which may be mentioned as responsible for effecting this change are:

First. A large quantity of solid residue after the ignition of a charge.

Second. The volume of black smoke caused by the presence of a large quantity of noncombustible material.

Third. The relatively great speed of erosion of the gun barrel due to the high temperature of combustion.

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Fourth. Rapid deterioration when exposed to atmospheric conditions due to its hygroscopic tendency.

On the other hand the manufacture of black powder is not technically complicated.

Owing to its sensitiveness unusual precautions must be observed in the manufacture.

MANUFACTURE.

Black powder is a mechanical or physical mixture of potassium nitrate, charcoal, and sulphur in the approximate proportions of 75, 15 and 10, varying percentages being used with varying effects. The saltpeter and sulphur should be of a very high grade commercial quality, should be practically free from chlorides and chlorates, and for practically all grades, the percentage of perchlorate should not exceed 0.5 per cent. Charcoal should be obtained from burning of peeled willow and alder, excepting for saluting and blank-fire powders, for which charcoal made from hard woods is used. Depending upon the use to which the particular grade is to be put the percentage composition of the finished material is altered as necessity demands. It has been found, for instance, that by increasing the percentage of saltpeter the rate of burning is increased; by increasing the percentage of charcoal the rate of burning is decreased. Extensive incorporation improves the quality and uniformity.

Purification of saltpeter is obtained by means of repeated recrystallization, the formation of large crystals being prevented by continuous agitation of the saltpeter liquor.

PROCESS.

The sulphur and charcoal in the proportions specified are pulverized at the same time in a ball mill, which consists of a revolving steel cylinder in which iron or steel balls do the crushing or grinding. This pulverized material is mixed either with pulverized saltpeter or stirred into a saturated solution of saltpeter, depending on the plant equipment.

There are three methods of mixing:

First. The French method, which is rarely used in this country. The pulverized saltpeter, charcoal, and sulphur are mixed and incorporated in a ball mill in which the revolving cylinder is of hardwood and part of the balls are lead composition and part lignum-vitæ.

Second. Dry mixing, in which the ingredients are blended by hand or by mechanical devices. In each of the above methods a small quantity of water is added.

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Third. Wet mixing, in which the pulverized sulphur and charcoal are stirred into a saturated solution of saltpeter at a temperature of about 265° F. The mass is then spread on a floor to cool, after which it is ready for incorporation. The lumps formed in the cooling are easily broken.

After mixing by either of the above methods, the material is spread on the bed of the wheel mills in quantities of 300 pounds per wheel mill. The wheels, weighing 8 tons each, rotate on the material for 3 hours at 10 rotations per minute. Edge runners keep the material worked toward the center of the tread of the wheels. Wheel cake or clinker formed during this operation is crushed or broken before pressing.

In order to obtain uniform ballistic results, it is necessary that the powder be of uniform density before granulation. The horizontal hydraulic press has been found to be the best type for this operation. The press plates, usually of aluminum, are so placed as to give press cake approximating three-fourths inch in thickness and about 24 inches square. The effective pressure on the press cake is estimated at 1,150 pounds per square inch.

The press cake is cracked or granulated in the corning mill by feeding the cake between crusher rolls. Mechanically operated shaking screens separate the dust and coarse grains from the finished grain—the coarser lumps passing through successive crushing rolls—four sets of crushing rolls being the usual number per mill. This operation is considered as the most hazardous of the various operations in the manufacture of black powder. Many devices have been employed to reduce the loss of property and life in the corning mill to a minimum. Most of these efforts have been toward conserving material that is lost, in the way of dust, and which during operation of the mill prevents the proper oversight of machinery or extraction of foreign substances in the powder; and the use of labor-saving devices and mechanism so arranged that the mill can be operated from a place of safety.

FINISHING.

There are three accepted standard processes for finishing:

First. In which drying and polishing are separate processes.

Second. In which drying and polishing are one operation.

Third. In which drying and polishing are one operation in a heated cylinder.

The rounding or polishing of the grain is accomplished by tumbling in a revolving wooden cylinder. The drying may be done in the same cylinder by forcing a current of warm air through the cylinder while the powder is being polished, or the powder may be removed from the cylinder and dried in stationary wooden trays. When

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heated cylinders are used the cylindrical surface of the revolving cylinder are steam jacketed, warm, dry air being forced through the cylinder as described above. The damage done by an explosion of a mill of this type leads to its abandonment. To glaze the polished grains a small quantity of pulverized graphite is added to the powder while the powder is hot from the tumbling or polishing process and the process continued for about half an hour.

The drying and glazing process, when carried out on the single operation plan, requires 8 hours.

PACKING.

Before packing, the powder is rescreened and separated into grades according to specification requirements. Containers for black powder are made of soft steel and average about 9 inches in diameter by 11 inches high, capacity 25 pounds, painted black, stenciled to show grades, lot number, maker, and contract number.

INSPECTION.

The various grades of black powder specified by the Ordnance Department are classified according to their percentage of composition, purity of material, size of granulation and rate of burning. For example, a certain latitude is permitted in the lower grades of black powder in the purity of the saltpeter and the percentage used in the finished product. Similarly the use of those grades of charcoal which yield a larger percentage of dust is also permitted. With grade "C" black powder, however, where the uniform rate of burning is of utmost importance, the inspection details are governed by more rigid specifications.

The different sizes of granulation form the basis for a secondary classification, as is indicated by the following table:

Powder.	Screens.	Passer.	Tolerances.	Duster.	Tolerances.
Army black powder:					
Grade A—		*Inches.*	*Per cent.*	*Inches.*	*Per cent.*
No. 1	Opening	0.185	3	0.093	5
	Mesh	4 to 1		8 to 1	
	Diameter	.065		.032	
No. 3	Opening	.065	3	.046	5
	Mesh	10 to 1		14 to 1	
	Diameter	.035		.025	
No. 4	Opening	.046	3	.0164	5
	Mesh	14 to 1		35 to 1	
	Diameter	.025		.0121	
Unglazed	Opening	.0328	3	.0164	5
	Mesh	20 to 1		35 to 1	
	Diameter	.0172		.0122	
Grade B	Opening	.131	3	.046	5
	Mesh	6 to 1		14 to 1	
	Diameter	.036		.025	
Grade C	Opening	.0041	3	.....	.....
	Mesh	150 to 1		.....	
	Diameter	.0026		.....	

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Use.—The general uses of these powders are as follows:

Designation.	Uses.
Army black powder:	
Grade A—	
No. 1	All igniting charges.
No. 3	All primers, except as noted for powder No. 4; 3.2-inch shrapnel head charges.
No. 4	Base charges for shrapnel; base charges for fuses; friction primers; model of 1914; obturation friction primer.
Unglazed	Unglazed, pellets for primers and fuses.
Grade B	All saluting charges.
Grade C	Time train rings of fuses; pellets for delayed-action fuses.

METHODS OF ANALYSIS.

Sampling.—About 50 grams of the original sample are crushed in small portions in a porcelain mortar and passed through an 80-mesh sieve. All precautions are taken to avoid unnecessary exposure of the sample to the air during this treatment. If each portion is placed in a stoppered bottle as soon as sifted, there is no appreciable change in hygroscopic moisture content. The powdered sample is well mixed before its analysis is begun.

Moisture.—About 2 to 3 grams of the powdered sample is spread in a thin layer on a tared 3-inch watch glass, carefully weighed and dried over sulphuric acid in a desiccator for three days or in a drying oven at a temperature of 60° to 70° C. to constant weight (about two hours). Cool in desiccator and weigh. Loss of weight is calculated as per cent moisture.

Potassium nitrate.—In the determination of potassium nitrate by extraction with water about 10 grams of the finely ground sample are weighed in a Gooch crucible with asbestos mat and about 200 c. c. of water, in successive portions of 15 to 20 c. c. each, is drawn through the sample by means of suction. The complete solution of the nitrate is hastened by the use of warm or hot water, although 200 c. c. of cold water is usually sufficient. The final portions of water passing through the crucible should be tested for soluble nitrate by evaporation on a glass plate, or an excess of strong sulphuric acid containing a few crystals of diphenylamine may be added to a few drops of the water, and an intense blue coloration will indicate the presence of nitrate.

The extraction is made on duplicate samples. After the complete removal of the nitrate the crucibles containing the portion insoluble in water are placed in a drying oven at a temperature of about 70° and dried to constant weight, usually overnight, although five hours is generally sufficient. The percentage of loss of weight, minus the moisture content found as described above, represents the total water-soluble material, and includes, in addition to sodium or potassium nitrate, a small amount of water-soluble organic material from

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the charcoal and the impurities in the original nitrate, such as chlorides and sulphate. As a check on this result an aliquot portion of the water extract may be evaporated to dryness on a steam bath, treated with a little nitric acid, again evaporated, heated to slight fusion, and weighed.

Sulphur.—The dried and weighed material left from the extraction with water consists of the sulphur and charcoal. The sulphur is determined by loss of weight on extraction with carbon disulphide in the Wiley extractor, or other suitable extraction apparatus, drying the insoluble residue to constant weight at about 100° C.

Before drying this residue in a hot oven, the carbon disulphide should first be allowed to evaporate by placing the crucibles in a warm place away from any flame or other source of high temperature, as the vapors of carbon disulphide are very inflammable.

The sulphur used in black powder should be brimstone, the flowers of sulphur not being suitable on account of the invariable presence of acidity. If flowers of sulphur are present, the extraction with carbon disulphide will be incomplete, due to the presence of insoluble amorphous sulphur. In this case it is necessary to resort to extraction with hot aniline in order to remove all of the sulphur, pouring 80 to 100 c. c. of aniline heated to 130–135° C. through the crucible in 10 c. c. portions, finally sucking dry, washing with a little alcohol to remove all of the aniline, drying and weighing.

Charcoal.—The residue left from extraction of the sulphur is the charcoal, which is weighed direct as already noted.

Ash.—The ash of the charcoal is determined by ignition of the insoluble residue over a Bunsen burner until all of the carbon has been burned off, and weighing. The ash usually amounts to about 0.5 to 1 per cent of the total powder. An unusually high value for ash may indicate incomplete extraction with water.

Specific gravity.—Weigh 10 grams and transfer to a strong 50 c. c. specific gravity bottle with a perforated glass stopper. Fill the bottle one-half to two-thirds full with clean mercury. Place under vacuum and fill the remaining space with mercury. Weigh the bottle containing the powder and mercury at 19° to 21° C. The actual weight of the bottle plus mercury, plus powder, subtracted from the gross weight of bottle full of mercury, plus the powder taken at 19° to 21° C., represents the weight of mercury displaced. This weight divided by the specific gravity of mercury at 19° to 21° C. (13.59) gives the weight of an equal volume of water. The weight of the powder used, divided by this weight of water, represents the specific gravity of the powder.

NOTE.—To displace the air from the specific gravity bottle, attach a piece of heavy rubber tubing about 2 feet long to the bottle. Attach the other end of the rubber tubing to one leg of a Y tube. Extend the other leg of the tube by

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means of a small piece of glass tubing and rubber tubing to dip into a vessel containing mercury. The stem of the Y is connected with the suction line. Close the rubber tube leading to the mercury vessel by means of a pinch cock. Turn on the suction and evacuate the specific gravity bottle, then close the suction line by means of a pinch cock placed close to the specific gravity bottle. Open the pinch cock on the tubing leading to the mercury vessel and allow the mercury to flow into the specific gravity bottle. Repeat this operation until the bottle is filled with mercury.

Determination of granulation.—Weigh out accurately 65 grams of the powder, empty it into the passer screen and shake vigorously over a sheet of brown paper for exactly one minute. Set aside the powder which has passed through the screen. Empty the material remaining in the sieve onto the sheet of brown paper, striking the screen sharply with the fingers to remove any adhering powder grains. Again sift the material so obtained for exactly one minute, again empty the sieve, again removing any grains adhering to the mesh, and submit the material to a third sifting. Collect the material which has now failed to pass through the screen, weigh it to the nearest tenth of a gram, and calculate the percentage of powder which failed to pass through the passer screen. Empty onto the duster screen all the material which has been used in the passer-screen test, sift through three times as described above, collecting each time the material which passed through the screen, bring this material together, weigh it, and calculate the percentage of powder which passed through the duster screen.

Moisture and ash free analysis.—Percentages on a moisture and ash free basis are calculated, by dividing the percentages of potassium nitrate, sulphur and carbon, respectively, by the remainder obtained by subtracting the sum of the percentages of moisture and ash from the sum total of the percentages obtained for potassium nitrate, sulphur, carbon, moisture and ash.

Determination of potassium.—Potassium may be determined by the perchlorate method. This method depends upon the fact that potassium perchlorate is practically insoluble in alcohol, whereas the perchlorates of the other bases which might be present are more or less readily dissolved by this solvent. The water solution containing potassium salts must be free from sulphuric acid or sulphates; if it does contain them they can be removed by precipitation with $BaCl_2$, and filtration. The solution is then evaporated to dryness and all acid fumes and ammonium salts driven off. The residue is dissolved in 50 c. c. of hot water containing considerably more than enough perchloric acid to combine with all the bases. Usually 5 to 6 c. c. of perchloric acid solution of 1.12 specific gravity is sufficient. This solution is obtainable from chemical dealers. Evaporate the mixture until it is thick, add a little more hot water and 5 to 6 c. c.

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more of the perchloric acid, and continue the evaporation, with stirring. Then heat the residue on a sand bath until dense white fumes are evolved. The cooled residue is then stirred with 20 c. c. of 97 per cent alcohol containing 0.2 per cent by weight of perchloric acid, and transferred to a Gooch crucible, using 20 c. c. more of the same alcohol solution. The residue of potassium perchlorate in the Gooch crucible is then washed with about 20 c. c. of a mixture of equal volumes of ether and alcohol, dried at 120° to 130° C., and weighed. The barium perchlorate is readily soluble in the alcohol used, and magnesium does not interfere if the excess of perchlorate acid is large enough. Ammonium salts should be removed, as has been stated, because ammonium perchlorate is not readily soluble in alcohol.

Chlorides, chlorates, and perchlorates.—Chlorides, chlorates, and perchlorates are identified as follows: Some of the solution in water is acidified with a few drops of nitric acid, an excess of silver nitrate added, the mixture heated to boiling, shaken well to coagulate the precipitate of silver chloride, and filtered. To the clear filtrate a few cubic centimeters of formaldehyde (40 per cent solution) is added and the mixture is then boiled. The formaldehyde reduces any chlorate present to chloride, which is precipitated as silver chloride by the excess of silver nitrate present. The reaction is practically complete if the mixture is allowed to stand on the steam bath for about an hour, although a considerably longer time is required for quantitative reduction. The precipitate is filtered off and the filtrate evaporated to dryness to remove excess of nitric acid, transferred with a small volume of water to a crucible, enough dry sodium carbonate added to fill the crucible, the mixture dried carefully over a burner, and fused. The fused mass is dissolved in dilute nitric acid. If perchlorates are present, the solution will be found to contain a precipitate of silver chloride.

BLACK-POWDER STORAGE.

In the consideration of the storage of low explosives, of which black powder is an example, it must be remembered that these materials are particularly sensitive to flame or spark. The restrictions, then, relative to the carrying of matches, to the cleanliness of the floors of magazines, to smoking, and to the use of nonsparking tools in general, should be rigidly enforced and carefully supervised. It is advisable also when working in the magazines where black powder is stored to wear rubber-soled shoes, the so-called "powder shoes." When it becomes necessary to open a box or container of black powder it should always be done with a wooden wedge and mallet, at

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least 100 feet from the nearest magazine, and in a place which is protected from rain or direct sunlight. No metal tools of any description may be used. If it becomes necessary to repair a magazine, all explosives should be removed to a safe distance before work is started.

Black powder should preferably be stored in a magazine constructed of tile walls filled with sand. It should not be stored in the same building with dry picric acid, dynamite, or other high explosive. The kegs may be placed in the magazine either on their ends or sides.

In view of the fact that black powder has a tendency to absorb moisture, which causes deterioration and seriously affects the properties of the powder, it is important that the storage magazines be dry and well ventilated.

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PART II.—MILITARY HIGH EXPLOSIVES.

INTRODUCTION.

When the entire field of high explosives is considered, the term "military high explosive" has a restricted application to a relatively small number of substances. In determining the suitability of a high explosive for military use, careful consideration must be given to its various properties, including not only its strength but also its sensitiveness to shock or friction such as may occur in loading, its ability to withstand the shock of set-back in the gun, or, in the case of drop bomb explosives, ability to withstand penetration by bullets, its stability, hygroscopicity, action on metals, etc.

These various requirements, together with questions of availability of raw materials, have excluded many high explosives which may be used successfully for commercial purposes.

In the case of some of the explosives discussed herein, details of manufacture are not described, as such data is regarded by the manufacturers as confidential.

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CHAPTER VII.

TRINITROTOLUENE (T. N. T.).

GENERAL.

The importance of this explosive is based, first, upon its relative safety in manufacture, loading, transportation, and storage; second, on the fact that it is not hygroscopic; third, on the lack of any tendency to form unstabled compounds with metals, and finally upon its powerful, brisant, explosive properties.

Although trinitrotoluene was known as early as 1863, it was first suggested as an explosive only about 1890, but its importance from a military standpoint dates only from 1904. Since this time it has appeared as the principal constituent of many explosives and has been used by itself under such various names as triton, trotyl, tolite, trilite, trinol, tritolo, etc. It is commonly known in this country by the abbreviation T. N. T. The term trinitrotoluol, which is more generally used than trinitrotoluene, is less correct from the chemical point of view than the latter.

PROPERTIES.

T. N. T. usually resembles in appearance powdered maple or brown sugar, although in different grades of refinement or purity its color and appearance vary. When pure it is a crystalline powder of light yellow color. It dissolves readily in ether, acetone, alcohol, and various other solvents, but it is practically insoluble in water.

Depending upon its purity, T. N. T. is classified by Ordnance Department specifications into three grades, designated as follows:

Grade I, with a solidification point of at least 80.5° C.
Grade II, with a solidification point of at least 79.5° C.
Grade III, with a solidification point of at least 76° C.

Grade III is obtained directly by the nitrating process as described below, while Grades I and II must be prepared by recrystallization or special chemical treatment of Grade III material.

All grades of T. N. T. are poisonous under certain conditions and it is necessary that proper precaution be taken by those engaged in its manufacture or handling to avoid inhaling the vapors or dust from the hot or crystalline material. Good ventilation in manufacturing or shell-loading plants is highly essential, and personal

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cleanliness should be enforced upon the workmen. All clothing should be changed upon the beginning and completion of work.

T. N. T. is one of the most stable of high explosives, and when properly purified may be stored over long periods of time without alteration. It is quite insensitive to blows or friction but can be detonated by severe impact between metal surfaces. When ignited by flame it burns rapidly without explosion. Rapid heating of large quantities, especially in closed vessels, may, however, cause violent detonation. It should, therefore, be melted only in water or in steam jacketed melting kettles and never subjected to such temperatures as may result from the use of a free flame.

T. N. T. has an important advantage over picric acid in the fact that it has no tendency to form compounds to react with metals, thereby producing sensitive salts. It will, however, react with alkalies, such as sodium hydroxide or sodium carbonate, to form unstable sodium salts which are quite sensitive. For this reason the use of alkalies in the purification of T. N. T. is not permissible.

T. N. T. in crystalline form detonates readily under the influence of a No. 6 detonator (containing 1 gram of mercury fulminate). When compressed to a high density it requires a No. 8 detonator (containing 2 grams of mercury fulminate), and when cast it is necessary to employ a booster charge of crystalline T. N. T., tetryl, or other more sensitive explosive, to insure complete detonation.

The decomposition of T. N. T. on explosion may be regarded as occurring according to one of the following reactions, or more likely to a combination of both:

$$2\ C_6H_2(CH_3)(NO_2)_3 = 12\ CO + 2CH_4 + H_2 + 3N_2$$

or

$$2\ C_6H_2(CH_3)(NO_2)_3 = 12\ CO + 5H_2 + 3N_2 + 2C$$

The deficiency in oxygen as indicated by both of these reactions is always apparent from the black smoke produced by the explosion of T. N. T. This deficiency of oxygen may be compensated for by the addition of such substances as ammonium nitrate or sodium nitrate in various proportions, the resulting mixtures being designated as amatol and sodatol, respectively.

Like nitroglycerine dynamite, T. N. T. may be classed as a "quick acting" explosive. It detonates at a rate varying from about 17,000 feet per second for loosely compressed material to nearly 25,000 feet per second for material cast or compressed to its maximum density. Forty per cent dynamite has a rate of detonation of about 15,000 feet per second. Various other tests such as the ballistic pendulum test and the Trauzl lead block test show T. N. T. to be, in general, somewhat stronger and quicker in action than 40 per cent dynamite.

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MANUFACTURE.

The manufacture of T. N. T. involves the following processes:

First. Nitration of toluol to mononitrotoluol.

Second. The further nitration of the mononitrotoluol to the dinitro and finally to the trinitrotoluol.

Third. Washing the finished product until free of acid.

Fourth. Purification by remelting and chemical treatment or recrystallization.

Fifth. Granulation, screening, and drying.

The process of nitration of the pure toluol with a mixture of nitric and sulphuric acids may be carried out in various ways, for example:

(1) The one-stage process, where a large excess of a strong mixed acid is used and the temperature gradually raised, with the result that trinitrotoluol is produced in the one process without transfer or separation of spent acid from intermediate products.

(2) The three-stage process, where, by the use of three different acid mixtures and different conditions of temperature, etc., there are successively produced mono-, di-, and trinitrotoluol, each stage being carried out in a different nitrator.

(3) The two-stage process, where either mono- or dinitrotoluol is produced in the first stage and trinitrotoluol in the second.

The nitrator used for the single-stage process consists of a cast-iron or steel cylindrical tank having a capacity of about 1,000 gallons, equipped with a steam jacket and cooling coils. The agitation in the kettle is effected by means of baffles fastened to the side of the tank operating against a mechanically driven propeller. The mixed acid used consists of approximately 76 per cent H_2SO_4 and 23 per cent HNO_3. After the acid has been blown into the nitrator its temperature is reduced to 30° C. and the charge of toluol slowly run in by gravity. It takes about one hour and a half for the complete addition of the toluol, during which time care is observed to keep the temperature between 30° and 50° C. Finally the steam is turned on and the temperature gradually raised over a period of several hours until a maximum of 110° C. is reached, at which temperature the charge is "cooked" for about three hours. A sample is then taken and a determination made of the solidification point. If this is below 70° it is necessary to cool the charge and add an additional amount of mixed acid. This procedure is continued until the test shows that the conversion of the dinitro to the trinitro has been completed.

In the two and three stage processes of nitration a different procedure is carried out and the nitration of the toluol to the mono-oil is effected by utilizing the spent acid recovered from a previous nitration. In fact, the nitration process consists on the one hand of

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the progressive nitration of the material, and on the other of the progressive denitration of the acid by utilizing the spent acid from the next higher nitration. In other words, the strongest acid is used for the third nitration. This strong acid consists of a mixture of fuming sulphuric acid and strong nitric acid.

The process is very similar to that employed for the one-stage process with the exception of the method of addition and separation of the acids. The mononitration is first accomplished by running into the nitrator a charge of spent acid from previous dinitration fortified to the proper HNO_3 content. The toluol is then added in approximately the same proportion, with continual stirring. This first nitration period is usually about 1 hour and 20 minutes and the temperature is maintained below 150° F. At the end of the operation the mixture of spent acid and mononitrotoluol is allowed to stand until the two constituents have separated enough so that the acid may be drawn off. The mono oil is then blown over to another nitrator, where it is subjected to a second nitration similar to the one just completed, except that in this case the spent acid is that from the trinitration, properly fortified to the required HNO_3 content. The dinitrotoluol resulting from this process is usually given the third nitration in the same nitrator, using a strong mixed acid as already noted. The separation of the finished product from the spent acid is effected by gravity, the spent acid being adjusted for use in the next lower nitration as above indicated.

The residue of mother liquors obtained from the di- and trinitrotoluols possesses the property of colloiding with pyro cotton in a manner somewhat similar to that of nitroglycerine, and this property is made use of by certain manufacturers for the manufacture of certain classes of sporting powders.

Humphrey (Jour. Ind. Engng. Chem., v. 8, November, 1916) states that, contrary to the usual belief, the yield of T. N. T. from the di or second nitration, at a given temperature, is not the function of the water content of the mixture (except that too strong an acid tends to oxidize the material and in this manner lowers the percentage of yield), but is rather dependent upon the proper low temperature during nitration. The mono nitration yields a product containing a mixture of about 4 per cent of the meta nitrotoluol in addition to the ortho and para isomers. The subsequent nitration changes the meta mononitrotoluol into the beta and gamma trinitrotoluenes, which differ from the alpha form in chemical properties and are regarded as impurities. Depending upon the completeness with which the last nitration is peformed there may be either a large amount of dinitrotoluene present if improperly carried out, or, if correctly done, a relatively small amount.

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In addition to these impurities, there may also be such bodies as tetranitromethane which possesses the undesirable property of lowering the settling point of the pure alpha T. N. T. If the nitration has been properly carried to completion, there should not be present more than 4 per cent beta and gamma T. N. T. This condition is not usually attained under manufacturing conditions and it is, therefore, necessary to recrystallize and repurify the T. N. T. in order that the impurities may be eliminated, and a product of the required setting point for Grade I, T. N. T. (80.5° C.), obtained.

PURIFICATION.

The crude trinitrotoluene, which, due to the heat of reaction, is in the form of an oil, is run from the nitrator into neutralizing tubs which have the shape of a cone at the bottom. At the apex of the cone a gateway valve for regular discharge from the tub is provided. Steam coils for heating and air coils for agitation are both provided. Wash water is drawn off by means of suction through a suitable pipe which reaches the tub near the top and extends along the side wall to about 2 feet from the bottom. A small quantity of sodium sulphite can be used to assist in the purification at this point, although it is not necessary to do so. Washing is carried on until no test for acidity is shown by the use of litmus paper. The neutral T. N. T., in the form of oil, is now pelleted by running into cold water, for transportation to the graining house, or can be transported in the molten condition to suitable storage tanks through heated pipe lines. If pelleted, these pellets are transported to storage tanks, as above mentioned, and again melted before running into the crystallizing kettles. The storage tanks are kept at an approximate temperature of 95° C., and are provided with a gateway screw valve from which the molten charge is drawn off into the graining kettles. These kettles are made of cast iron, in one piece, and the junction of the bottom and the side walls is rounded so that plows can scrape the T. N. T. loose from the sides. The lower part of the kettle is fitted with a jacket into which steam or cold water may be discharged. As the plows are started, the charge cools down and the crystals begin to form on the sides which increase until the whole mass becomes plastic. During the operation all moisture is driven off and the T. N. T. produced is in a fine crystalline condition. The T. N. T. produced is usually better than Grade III, which is 76° melting point. If it is desirable to obtain T. N. T. of Grades I and II, recrystallization from either alcohol or sulphuric acid or a treatment with sodium sulphite must be made. A brief description of each is given below.

Crystallization from sulphuric acid.—The fine crystals produced in the graining kettles are dissolved in hot sulphuric acid, usually

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weight for weight, and cooled. The purified crystals thus settling out are washed free from acid and regrained to such a degree of fineness as to pass Ordnance Department specifications. The crude material held in sulphuric acid is accumulated until such time as the amount warrants separate purification.

Crystallization from alcohol.—The fine crystals of T. N. T. are dissolved in warm 95° alcohol denatured with benzene. This alcoholic solution is filtered and cooled, and sufficient alcohol is distilled off to cause T. N. T. of setting point of not less than 80.5° to separate out. This distillate is recovered and used over again. The crude T. N. T., commonly known as "still residues," is usually used up in the manufacture of commercial explosives.

Sulphite purification.—The sodium sulphite treatment is usually applied by taking the fine crystals from the graining kettles, placing them in bins or cars which are equipped with a Filtros bottom. These bins or cars are given one hot water washing, then four washings with the 5 per cent solution of sodium sulphite, then one warm water washing followed by sufficient cold water washings to remove the last traces of the red color which is formed in the treatment. The purified crystals thus obtained can be dried, sieved, and packed, or regrained, as may be necessary to meet specifications.

USE.

Grade I T. N. T. is considered more expensive than Grades II and III, because it requires additional purification; it is therefore used only in boosters for high-explosive shell, where the best grade of material is required. Grade II is used as the bursting charge for high-explosive shell, either alone or mixed with an equal weight of ammonium nitrate to form 50/50 amatol (the T. N. T. in either case being melted so that the shell is filled by a casting or pouring process). Grade III is used only in 80/20 amatol, where it is mixed in the molten state with four times its weight of ammonium nitrate and filled into high-explosive shell by hand stemming or by means of a screw filling machine.

A charge of about 1⅔ pounds of cast T. N. T. in a 75-mm. high-explosive shell weighing about 9½ pounds breaks up the shell into approximately 700 fragments.

Other military uses for T. N. T. are as a bursting charge for hand grenades, rifle grenades, aeroplane drop bombs, naval submarine mines, and depth bombs. In aeroplane bombs it has the disadvantage that penetration of the bomb by a rifle bullet may cause an explosion of the charge. This is also true of amatol, which has been used more extensively than T. N. T. in drop bombs. When used in grenades, the crystalline Grade II, T. N. T., is loaded by means of vi-

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brators which "jolt" the grenades until they are completely full. Grade III is suitable for mines or drop bombs and is loaded by casting, as in the case of high-explosive shell.

T. N. T. is also used for military purposes in demolition work on bridges, railroads, etc., and for land mines placed under enemy trenches or fortifications. For demolition work carried on by the Engineer Corps the T. N. T. is made up in the form of small, highly compressed blocks which are graphited on their surfaces and then copper plated; this protects them from crumbling in handling and renders them waterproof.

T. N. T. has been demonstrated to be suitable for all kinds of blasting work where 40 per cent dynamite is used, and to give practically equal effects. It is well adapted for "adobe" shooting or "mud capping," terms applied to the breaking up of large rocks or bowlders by means of a charge of high explosive placed on the rock and confined only by means of a shovelful of mud or wet earth thrown over it. Only quick-acting explosives can be successfully used for such work. Even in drill holes containing water, T. N. T. gives excellent results because of the fact that it is insoluble in water. Its use for blasting has, however, been negligible because of the fact that military requirements have made it unavailable and expensive as compared with commercial dynamites.

On account of its ability to act as a "booster" in bringing about the detonation of more insensitive explosives, T. N. T. has been employed as a partial substitute for the mercury fulminate in commercial electric blasting caps or detonators. A charge of T. N. T. is pressed into the bottom of the cap, covered by a small priming charge of fulminate and the whole charge confined by a perforated copper capsule pressed on top of the priming charge. Such T. N. T. detonators have been extensively used abroad but have not met with great success in this country.

" Cordeau Bickford," a trade designation for detonating fuze, consists of a flexible lead tube, smaller in diameter than a lead pencil, filled with T. N. T. It is quite extensively used in certain blasting operations, especially for insuring the complete detonation of large charges of dynamite. The detonating fuze being passed through the entire length of the charge, and detonated at its external end by means of an ordinary blasting cap, transmits its high rate of detonation to the entire charge of dynamite.

INSPECTION.

Specifications.—The chemical and physical requirements prescribed by Ordnance Department specifications for the different grades of T. N. T. are as follows:

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	Grade I.	Grade II.	Grade III.
Solidification point — not less than.	80° C.	79.5° C.	76° C.
Ash—not more than	0.1 per cent.	0.1 per cent.	0.1 per cent.
Insoluble matter — not more than.	0.15 per cent.	0.15 per cent.	0.15 per cent.
Moisture—not more than.	0.1 per cent.	0.1 per cent.	0.1 per cent.
Acidity—not more than (as H_2SO_4).	0.01 per cent.	0.01 per cent.	0.01 per cent.
Color	Light yellow.	Light yellow.	
Fineness	30-mesh sieve, opening 0.0183 inch, wire 0.015 inch.	12-mesh sieve, opening 0.058 inch, wire 0.025 inch.	12-mesh sieve, opening 0.058 inch, wire 0.025 inch (or flake).

It will be noted that the three grades vary only in solidification point and fineness.

ANALYSIS AND TESTING.

The most important test in connection with the inspection of T. N. T. is the determination of its solidification point or "setting point." This temperature serves as an indication of the purity of the explosive, inasmuch as the presence of moisture, lower nitrating products, objectionable amounts of isomers, and other impurities all tend to lower the solidification point. In order, however, to insure the proper degree of purity, additional determinations of ash, insoluble matter, moisture, and acidity, are required by Ordnance Department specifications. The prescribed methods of conducting these tests are as follows:

Solidification point: The apparatus used consists of the following parts: A test tube 1 inch in diameter and 6 inches long is fitted through a cork into a second test tube 1½ inches in diameter and 7 inches long, which in turn is set into a large-mouth liter bottle. Into the inner tube is fitted a cork stopper through which are three openings. One is in the center for the standard thermometer, which should be graduated in 1/10° C. One is immediately at the side of the center hole and is for a small thermometer which is passed just through the stopper and which reading is taken as the average temperature of the exposed stem of the standard thermometer in making the stem correction. The third hole in the stopper is a small V-shaped opening at the side, through which passes a wire whose lower end is bent in a loop at right angles to the axis of the tube and which is used as a stirrer.

The test is carried out as follows: Place a 50-gram sample of T. N. T. in the inner tube and melt it in an oven, the inner tube being separated from the rest of the apparatus for this purpose. When the temperature has reached about 90° C. the tube is replaced in the apparatus, the standard thermometer placed so that the bulb is approximately in the center of the molten T. N. T., and the small side thermometer put in place. The stirrer should already be in

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the molten T. N. T. Stirring is continued vigorously as the temperature falls, and the thermometer must be watched very carefully. When a point is reached where the temperature begins to rise, owing to the heat of crystallization, readings should be recorded about every 15 seconds until the maximum temperature is noted. This temperature usually remains constant for several minutes until crystallization is complete, and observation should be continued until it is certain that the maximum temperature has been reached. This takes from 5 to 10 minutes after the beginning of crystallization. This maximum temperature with the correction for emergent thread is taken as the solidification point of the sample.

Ash: Burn a known weight, approximately 5 grams, moistened with sulphuric acid, in a tared crucible. To compensate for reduction of any metallic salts, add a few drops of nitric acid and sulphuric acid and again ignite and weigh.

Insoluble matter: Boil a known weight, approximately 10 grams, with 150 c. c. of 95 per cent alcohol. Filter while hot through a tared Gooch and wash with hot alcohol. Dry to constant weight at 100° C., cool and weigh.

Moisture: A known weight, approximately 5 grams, is exposed in a desiccator over sulphuric acid in a watch glass to constant weight.

Acidity: A known weight, approximately 10 grams of the sample, is melted and shaken with 100 c. c. of neutral boiling water and allowed to cool. The sample is then remelted and again extracted with 50 c. c. of neutral boiling water. The total water extract is cooled and titrated with N/10 sodium hydroxide, using phenolphthalein as an indicator. Calculate results as per cent sulphuric acid in the original sample.

Nitrogen: The determination of nitrogen is not required as a part of routine inspection and is only made in particular cases; e. g., where the solidification point is found to be unusually low. There are various modifications of the Kjeldahl method which give fairly accurate results with T. N. T.; e. g., the method described in Bureau of Mines Technical Paper No. 160. For accurate determinations, however, the Dumas combustion method is considered far more reliable if properly conducted.

Fineness: It is required that Grade I, T. N. T., should pass completely through a screen containing 30 mesh to the linear inch, the openings being 0.0138 inch and the wire 0.015 inch in diameter. Grades II and III are required to pass a 12-mesh screen having openings 0.058 inch and wire 0.025 inch.

STORAGE.

The type of magazine best designed for the storage of T. N. T. is similar to that used for ammonium picrate and wet picric acid. The

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buildings should not be larger than 26 by 42 feet and may be constructed of tile, asbestos protected metal, or tile walls filled with sand.

The cleanliness both within and without the magazine should be carefully watched and the same rules applied as in the case of the storage of smokeless powder. Special regulations, however, for this material are not necessary, as is the case, for instance, with black powder or picric acid. The loading of shells, by casting or by tamping, should be performed when necessary, as far from the magazine as is possible, and in no case less than 200 feet.

The use of the automatic sprinkler system in the magazines in which T. N. T. is stored has been recommended as protection against incipient fires by the National Board of Underwriters, the action of the sprinklers tending to prevent overheating and the subsequent possible detonation of large quantities of high explosives. (See Suggested Protection for Munition Magazines, National Board of Underwriters, Committee on Fire Protection and Engineering Standards, 76 William Street, New York City.)

The poisonous effects already mentioned as resulting from the handling of T. N. T. both in the manufacture and storage must be well considered and every precaution observed to protect the workmen at all times.

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CHAPTER VIII.

AMMONIUM PICRATE (EXPLOSIVE D).

GENERAL.

The use of ammonium picrate as an explosive was patented by Nobel in 1888 (Mosenthal, Jour. Soc. Chem. Ind., vol. 18, p. 447, May, 1899), although even prior to that time Brugere made use of a mixture of ammonium picrate and sodium nitrate as a propellant explosive.

The importance of ammonium picrate as a military explosive is due entirely to its marked insensitiveness to shock and friction, which makes it well suited for use as a bursting charge in armor-piercing projectiles. From the standpoint of explosive strength, however, this explosive is inferior to T. N. T.

PROPERTIES.

Ammonium picrate is soluble in water, crystallizing from its solution in orange-yellow needles, darker in color than picric acid. It resembles picric acid in its bitter taste and property of dyeing the skin, clothing, etc., of those engaged in its manufacture or handling.

It has a much greater tendency to absorb moisture than has picric acid, samples having been found to absorb over 5 per cent by weight of water during storage for one month in an atmosphere saturated with moisture.

Like picric acid, ammonium picrate can react with metals to form metallic picrates, but it reacts with much less readiness than picric acid; in fact, when dry its action is almost negligible. Wet ammonium picrate reacts slowly, especially with copper or lead, to form picrates, which are particularly sensitive and dangerous.

Ammonium picrate does not melt on heating, but explodes when heated to a temperature of about 300° C. Small traces of metallic picrates may, however, lower this ignition temperature appreciably.

Ammonium picrate is the least sensitive of all military explosives used as the bursting charge for shell. Its insensitiveness to shock accounts for it being given preference over T. N. T. or amatol as the bursting charge for armor-piercing, base-fuzed shell. It is also more insensitive to detonation by means of mercury fulminate than is T. N. T. Impact tests, made by dropping a weight on a small sample of the explosive spread between metal surfaces, show no very

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great difference in the sensitiveness of T. N. T. and ammonium picrate, but more reliable conclusions can be obtained by the results of actual firing of loaded shell against armor plate, whereby ammonium picrate is readily shown to be the least sensitive.

Ammonium picrate is slightly less powerful than T. N. T. The Trauzl test shows an expansion of approximately 240 c. c. from the former as compared with about 260 c. c. for T. N. T. This difference is, however, due to the fact that T. N. T. as used has a higher density than can be readily obtained with ammonium picrate. As a charge for high-explosive shell, T. N. T. is required to have a density of at least 1.55, while the specified density of ammonium picrate is 1.33 to 1.37. At equal densities ammonium picrate is slightly more powerful than T. N. T. At a pressure of about 12,000 pounds per square inch the two explosives have the same densities.

Like T. N. T. and picric acid, ammonium picrate liberates free carbon on explosion, giving a black smoke. These products of explosion, although more disagreeable in odor, are less poisonous than those from T. N. T. and picric acid, in that they contain less carbon monoxide.

MANUFACTURE.

The manufacture of ammonium picrate consists in the main of a simple neutralization of picric acid by means of ammonia either alone or in combination with ammonium carbonate. This process is not attended with any serious manufacturing difficulties or dangers, provided one excludes the possibility of leaking ammonia pipes. The details of manufacture are as follows:

Approximately 300 pounds of picric acid are mixed in 500 gallons of water at room temperature and then slowly heated by direct steam. As the mixture warms, aqua ammonia is added at the bottom of the tank until neutralization is completed. In some factories it is the practice to add a faint excess, thus insuring complete neutralization of all the picric acid, this condition being evidenced by the formation of a reddish colored crystalline mass of ammonium picrate. When this stage has been reached the resulting material is dropped into tanks for crystallization. These tanks are so equipped that a continual agitation of their contents can be maintained by air with the object of accelerating the crystallizing of the ammonium picrate during the cooling. When the mass has cooled to about 25° C. the crystals are separated from the mother liquor by filtering or draining. From the crystallizing tank the ammonium picrate is taken to the dry house where it is subjected to a temperature of about 45° C. for eight hours in drying bins which are so constructed that warm air circulates constantly through the mass. Finally the dried material is screened by means of a rotating barrel screen and

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sent directly to the packing room. The finished product is then packed in 50-pound boxes lined with waterproof paper and sent to storage.

REWORKING AMMONIUM PICRATE.

This operation consists in redissolving impure or waste ammonium picrate in water, removing the impurities by filtration, then heating the solution by steam coils until it has been evaporated sufficiently to produce crystallization. From here on the reworking operations are exactly the same as those followed out in the manufacture of the new material. The reworking of ammonium picrate is made necessary on account of the fact that when this material has once been subjected to heavy pressure, as is always the case in shell-loading operations, it is much more sensitive to detonation than new material. In this condition it is unsafe to load, inasmuch as continued repressing may result in detonation.

USE.

As has been mentioned, ammonium picrate is used as the bursting charge for armor-piercing shell on account of its superior insensitiveness to shock, which permits the shell to pass through the armor before exploding. Owing to the fact that it can not be melted without decomposing it must be loaded into the shell by hydraulic pressure or hand stemming. The interior of the shell is covered with a suitable nonmetallic paint or varnish and a moisture-proof seal provided around the booster at the base of the charge by means of cast T. N. T.

Ammonium picrate has also been used to some extent in France, mixed with potassium nitrate, as a propellant explosive for use in guns.

It has no commercial use as an explosive, although it enters into the composition of numerous patented blasting explosives which have not been used to any great extent.

INSPECTION.

Specifications.—Ordnance Department specifications prescribe the following chemical requirements for ammonium picrate:

It must not contain—

(*a*) Less than 5.60 per cent ammoniacal nitrogen.
(*b*) More than 0.20 per cent moisture.
(*c*) More than 0.10 per cent sulphuric acid (free and combined).
(*d*) More than traces of nitrates.
(*e*) More than 0.20 per cent insoluble material.
(*f*) More than 0.20 per cent mineral matter (ash).
(*g*) Free ammonia.
(*h*) More than 0.5 per cent nitro phenols.

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ANALYSIS AND TESTING.

The following tests and determinations are made on ammonium picrate to determine its suitability for military use:

Moisture: Dry a known weight, approximately 10 grams, thinly spread in a tared glass dish at 95° C. for two hours or to constant weight.

Insoluble material: Dissolve a known weight, approximately 10 grams, in 150 c. c. of hot distilled water, and boil for 10 minutes. Filter on a tared Gooch, wash thoroughly with hot distilled water and dry to constant weight at 100° C.

Ash: Saturate a known weight, approximately 1 gram, with melted paraffin and burn off carefully. Ignite the residue, cool and weigh.

Nitrophenols: A known weight, approximately 10 grams, of a finely ground sample is placed in a small beaker with 50 c. c. of chloroform and allowed to stand 30 minutes at room temperature with frequent stirring. Filter into a 100 c. c. tared flask, washing the residue with 25 c. c. of chloroform. Evaporate the filtrate to dryness on a steam bath and weigh residue. Dissolve the residue in distilled water and ammoniate. Evaporate the solution to dryness on the steam bath. Extract the residue with 22 c. c. of chloroform, filter and evaporate the chloroform filtrate to dryness in a tared dish and weigh. The difference in weight between the first chloroform extract residue and the second chloroform extract residue equals picric acid.

Ammoniacal nitrogen: A 1-gram sample of the ammonium picrate to be analyzed is placed in a 400 to 500 c. c. Kjeldahl flask. The flask is equipped with a two-hole rubber stopper which carries an exit tube, leading away to a bottle containing N/10 sulphuric acid, and an ingress tube, reaching to its bottom, through which air (that has already been dried and freed from ammonia by passage through concentrated sulphuric acid) may be bubbled; 20 c. c. of water are introduced into the flask, 12 c. c. of 5 per cent sodium carbonate solution are added, the flask is set in a boiling water bath and ammonia free air is bubbled through until the contents of the flask have been evaporated to dryness. The ammonia is absorbed by bubbling the air through 50 c. c. of N/10 sulphuric acid, a bulb full of very small holes, such as may conveniently be made with a hot platinum wire, being used for the purpose. To deal with the possibility of splashing of the sulphuric acid, the exit tube from the bottle is equipped with a trap. The excess sulphuric acid is titrated with N/10 sodium hydroxide, using methyl red or sodium alizarine sulphonate as an indicator, the amount which has been consumed is noted, and the ammoniacal nitrogen of the sample is calculated.

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Sulphuric acid: Dissolve a known weight, approximately 5 grams, in 100 c. c. of hot distilled water, filter and wash with 25 c. c. of hot distilled water. Acidulate with hydrochloric acid and heat, then add a hot solution of barium chloride with constant stirring, allow to settle and filter on a tared Gooch while hot; thoroughly wash with hot distilled water and dry to constant weight at 100° C. Calculate results as sulphuric acid in original sample.

Nitrates: Determine by testing a water solution of the sample with diphenylamine and concentrated sulphuric acid.

Free ammonia: Presence determined by titrating water solution with N/10 sulphuric acid, using methyl orange or sodium alizarine sulphonate as an indicator.

STORAGE.

The storage of ammonium picrate is governed by the same rules as are applicable for the storage of T. N. T., both as to type of magazine and rules for handling, and special regulations governing this particular explosive are not necessary. It is to be noted, however, that ammonium picrate which has been repressed at a shell-loading plant and removed from a shell is very much more sensitive to shock or blow than new material, and there are cases on record where serious accidents have happened in the loading of shells with ammonium picrate so treated. If it becomes necessary then to store this material, special precautions should be observed to protect it against a shock, or fire, and it preferably should be stored in a building by itself.

Although less sensitive than T. N. T. ammonium picrate can be exploded by severe shock or friction, is highly inflammable, and when heated to a high temperature may detonate. It is therefore necessary that it be treated with proper care as a high explosive.

Since it absorbs moisture it should be stored in dry magazines and protected from dampness. Moisture, however, has no effect on ammonium picrate except to reduce its explosive strength and its sensitiveness to detonation.

Ammonium picrate is always stored in wooden containers because of the possibility of its forming sensitive metallic picrates in contact with metals, especially when moist.

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CHAPTER IX.

PICRIC ACID.

GENERAL.

Picric acid or trinitrophenol was first adopted as a military high explosive by the French Government in 1886, under the name of melinite, and has since been used to a greater or less extent by almost all countries, with or without the addition of various materials intended to reduce its melting point or increase its strength. The British explosive designated as Lyddite, and the Japanese explosive Schimose, are both cast picric acid, and various names are given to other shell explosives, the chief component of which is picric acid.

The fact that picric acid readily forms dangerously sensitive salts with metals has practically precluded any extensive use of it as an explosive in this country, its present interest to the United States Government being that it is the raw material used in the manufacture of ammonium picrate.

PROPERTIES.

Picric acid is a lemon-yellow crystalline solid, only slightly soluble in water but soluble in alcohol, benzene, and other organic solvents. A very small amount is, however, sufficient to color a large volume of water a distinct yellow color. It likewise stains the skin of workmen, colors clothing, hair, and everything else with which it comes in contact, and has an exceedingly persistent, disagreeable, bitter taste. Its property of coloring is utilized in the dye industry, and, in fact, picric acid was long known as a dyestuff before its explosive nature was discovered. It has no tendency to absorb moisture from the air.

Picric acid melts at a temperature of about 122° C. when pure, and is usually required for explosive use to have a melting (or solidifying) point of at least 120° C. (248° F.).

Being an acid, it has the property of combining with ammonia and alkalies and with many of the metals, forming salts which are called picrates. Most of the picrates are much more dangerous than picric acid itself, and it is therefore necessary that metals be kept from direct contact with picric acid by means of suitable varnishes or lacquers. Tin is the only common metal which is not attacked by picric acid. Lead reacts so readily to form highly sensitive lead

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picrate, that it is necessary to entirely eliminate lead apparatus, pipe, etc., in the manufacture of picric acid and even in the manufacture of the nitric acid used in making picric acid.

Picric acid is a weak poison, the chief danger in connection with its use being probably the fumes given off from the molten explosive used in shell loading. Practically no trouble from poisoning results in the manufacture or handling of picric acid; care must be taken, however, to avoid the breathing of the large amounts of picric acid dust that may arise in screening or packing dry picric acid.

Picric acid is entirely stable if kept from contact with materials with which it can combine, such as alkalies or metals. It has no tendency to decompose at any temperatures which it might meet in storage. On sudden heating at temperatures much above its melting point (122° C.), it may explode, although many cases are noted where considerable quantities of picric acid have burned without explosion. The presence of any trace of explosive that will detonate more readily, such as metallic picrates, may cause the sudden detonation of burning picric acid.

It is somewhat more sensitive to shock or friction than T. N. T., and more readily detonated by means of a detonator. For such reasons, transportation regulations require that for bulk shipment picric acid must contain at least 10 per cent of water, because in this condition it is regarded as an inflammable only. Wet picric acid is, of course, thoroughly dried before use for explosive purposes.

Picric acid is one of the most powerful of military explosives. Its high strength or concussive effect is due to its high rate of detonation, which, for the cast or highly compressed explosive, is about 25,000 feet per second—slightly greater than that of T. N. T. under the most favorable conditions. By both the Trauzl lead block test and the ballistic pendulum test, picric acid shows appreciably greater strength than T. N. T., being exceeded only by tetryl and T. N. A. The results of these methods of testing are confirmed by actual fragmentation tests of high explosive shell, where it is found that a larger number of shell fragments is produced from picric acid than from T. N. T. at equal loading densities.

MANUFACTURE.

The raw material from which picric acid is derived is benzene (often called benzol). This substance must not be confused with benzine, which is essentially gasoline, obtained by the distillation of petroleum. Benzene is an inflammable liquid obtained as a by-product in the manufacture of coke by recovery from illuminating gas or by "cracking" oils at high temperatures.

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Picric acid may be manufactured from benzene by three distinct processes, designated respectively as the phenol process, the chlorbenzol process and the catalytic process.

Phenol process.—Practically all of the picric acid produced in this country during the war was made from phenol (carbolic acid). Phenol is prepared from benzene as a raw material by first treating pure benzene with strong sulphuric acid and heating the mixture in jacketed iron kettles provided with agitation at a temperature of about 90° C. (194° F.) for several hours. The resulting benzene sulphonate is usually treated with lime, which converts it to calcium benzene sulphonate, which, in turn, is converted to sodium benzene sulphonate by means of sodium carbonate (soda ash). The sodium benzene sulphonate is dried and heated in fusion kettles with caustic soda which converts it into sodium phenate. The fusion mixture is dissolved in water and treated with either carbon dioxide or sulphuric acid, which causes the phenol to separate out as a distinct layer. This layer is drawn off and distilled in order to separate the pure phenol from water and other impurities. Pure phenol is a white crystalline solid which melts at about 40° C. (104° F.).

For conversion to picric acid the phenol is melted into large jacketed iron kettles and treated with sulphuric acid of about 93 per cent strength, the mixture heated with stirring at a temperature of about 95° C. (203° F.) from four to six hours. The resulting phenol sulphonic acid is diluted with water and treated in a large acid-proof, brick-lined nitrator with 42° Baumé nitric acid (about 70 per cent). The reaction generates heat, and the mixing is therefore carried on very slowly, the maximum temperature being about 110° C. After cooling the mixture the crystallized picric acid is separated from the spent acid on a vacuum filter, washed with water, and dried.

Chlorbenzol process.—Although this process has been quite extentively used abroad, its use in this country has been rather limited. Briefly the process involves, first, the treatment of benzene with gaseous chlorine, whereby monochlorbenzene results. This product is purified by distillation, and then nitrated with a mixture of nitric and sulphuric acids to give dinitrochlorbenzene. The latter on treatment with lime or soda loses its chlorine and becomes calcium or sodium dinitrophenolate, which on acidifying is converted to dinitrophenol. The dinitrophenol is readily nitrated to picric acid (trinitrophenol) by means of nitric and sulphuric acids.

Catalytic process.—The catalytic process is only in its experimental stage in this country. It consists in converting benzene into either dinitrophenol or picric acid direct in one operation by means of weak nitric acid in the presence of mercury nitrate which acts as a catalyst. The weak nitric acid first oxidizes the benzene to phenol, which then combines with nitric acid to give di- and tri-nitrophenols.

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USE.

The fact already noted, that picric acid combines readily with practically all metals to form picrates which are unduly sensitive to friction, shock, or heat has been detrimental to the use of picric acid for military purposes, in spite of the fact that it is a stronger explosive than T. N. T. When a non-metallic lining is used for the shell cavity, as for instance, certain lacquers, varnishes or paints, the danger of the formation of these salts is obviated to a great degree. It may be mentioned in this connection that picric acid has certain distinct advantages over ammonium picrate, for example, while the repressing of ammonium picrate is a dangerous practice, with picric acid the contrary is the case, for the insensitiveness is increased within certain limits. The introduction of T. N. T. as a military explosive has resulted in the gradual abandonment of picric acid by practically every country except France, where it has been very largely used during the war. In the United States it has been used only for conversion into "explosive D" or ammonium picrate, which is largely used in base-fuzed shell for seacoast cannon. Picric acid has also found use as a booster explosive and even as a substitute for part of the mercury fulminate charge in detonators. It has been used to a limited extent as a component of many explosive mixtures proposed or patented for military or commercial use.

INSPECTION.

Specifications.—The chemical requirements prescribed for picric acid by Ordnance Department specifications are as follows:

It must have a solidification point of not less than 120° C.

It must not contain—

(*a*) More than 0.2 per cent moisture if purchased as dry picric acid or 12 per cent if purchased as wet picric acid.

(*b*) More than 0.1 per cent sulphuric acid, both free and combined.

(*c*) More than 0.2 per cent ash.

(*d*) More than 0.2 per cent matter insoluble in water.

(*e*) More than 0.0004 per cent soluble lead.

(*f*) Free nitric acid.

Color, lemon yellow.

Fineness, 12 mesh (screen openings 0.058 inch, wire 0.025 inch).

Analysis and testing.—The methods prescribed for testing are as follows:

Solidification point: A sample of the picric acid to be used for this test must be dried to constant weight at a temperature not exceeding 50° C. The sample is melted in a test tube 6 inches long and three-fourths of an inch in diameter, immersed in a bath of glycerine. Sufficient picric acid is taken to give a 3-inch column

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of the molten material in the test tube. The glycerine bath is kept at a temperature of 130° C. A standardized thermometer graduated in 0.1 of a degree is placed in the tube when the picric acid is completely melted and the tube removed from the glycerine bath and stirred until sample solidifies. At this point the temperature will remain constant for an appreciable length of time and finally slightly rises. The highest temperature reached on such rise is noted as the solidification point.

Moisture: Dry a known weight, approximately 10 grams, spread thinly on a tared watch glass or dish, 4 hours at 70° C., or to constant weight.

Sulphuric acid: Dissolve a known weight, approximately 2 grams, in 50 c. c. of distilled water. Acidify with hydrochloric acid, and then heat. Add hot barium chloride solution slowly with constant stirring and filter while hot on a tared Gooch. Wash thoroughly with hot distilled water, dry to constant weight at 100° C., and weigh. Calculate results as sulphuric acid in original sample.

Nitric acid: Test a water solution of picric acid with a solution of diphenylamine in concentrated sulphuric acid. No coloration should result.

Ash: Weigh a sample of approximately one gram in a platinum crucible, saturate with melted paraffin, and burn off cautiously. Ignite residue, cool and weigh.

Insoluble matter: Dissolve 10 grams of the sample in 150 c. c. of boiling water, continue boiling for 10 minutes, filter while hot through a tared Gooch, wash thoroughly with hot water, and dry to constant weight at 100° C.

Soluble lead: Place a known weight, approximately 300 grams of the picric acid, in a 2-liter flask and allow to soak in 100 c. c. of a hot saturated solution of barium hydroxide in 65 per cent alcohol. Shake well and add 1,400 c. c. of 95 per cent alcohol and digest at a temperature below the boiling point of alcohol until all the picric acid has been dissolved with the exception of small particles of insoluble matter. Shake the solution thoroughly and allow to stand in the cold until most of the picric acid has crystallized out, and filter. It is not necessary to disturb the crystalline picric acid at the bottom of the flask as only 500 c. c. of the solution is used for the completion of the tests and this amount can be decanted. Take 500 c. c. of this filtered solution which represents 100 grams of picric acid. Add 4 or 5 drops of nitric acid and 10 c. c. of a 1 per cent mercuric chloride solution and pass a slow stream of hydrogen sulphide through this solution for 15 minutes. Allow to settle 20 minutes, filter and wash with alcohol saturated with hydrogen sulphide. Dry the filter paper and ignite in a porcelain crucible. Add 9 c. c. of

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nitric acid, specific gravity of 1.42, and warm on a hot plate. Then add enough warm water to make up the volume to 50 c. c. Electrolize at 0.4 ampere and 2½ volts, temperature 65° C. After one hour, wash electrode by replacing the beaker with another one full of distilled water without interrupting the current. Dry and weigh the tared anode. The weight of lead peroxide found by difference multiplied by 0.8661 gives the per cent of soluble lead.

STORAGE.

The rules governing the storage of dry picric acid are the same as those which apply to the storage of black powder, dynamite, and dry guncotton. Wet picric acid being considered less hazardous, falls under the same classification as T. N. T. and ammonium picrate. The dimensions of the magazines in either case should not exceed 42 by 26 feet. They should be of the ordinary hollow tile construction, and the walls in the latter case (that of wet picric acid) filled with sand. It is necessary that all dust accumulating from dry picric acid should be carefully removed from any point in or around the buildings, conveyers, or cars. Although dust originating from this source is not as dangerous as that from black powder, it is nevertheless a matter of record that serious explosions have been caused from this source. Powder shoes must be worn in every instance where dry picric acid is being handled.

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CHAPTER X.

NITROSTARCH EXPLOSIVES.

GENERAL NATURE.

Under this classification are included "Trojan grenade explosive," "Trojan trench mortar shell explosive," and "grenite." These explosives are frequently referred to as "nitrostarch," but it should be noted that up to this time pure nitrostarch has not been used as either a military or a commercial explosive, the nearest approach to it for military purposes being "grenite," which is about 95 per cent nitrostarch with the addition of binding material added for the purpose of granulating. The two Trojan explosives, which are practically identical in composition, contain only approximately 40 per cent nitrostarch, together with ammonium nitrate, sodium nitrate and small amounts of materials added for the purpose of stabilizing, reducing sensitiveness and hygroscopicity, and neutralizing any possible acidity of other ingredients.

REASONS FOR ADOPTION.

These nitrostarch explosives were adopted by the Ordnance Department mainly for the reason that at the time the United States entered the war a decided shortage of T. N. T., owing to deficient toluol supply, was indicated. A thorough investigation showed that nitrostarch explosives, properly manufactured, seemed to be not only entirely suitable for trench warfare purposes, but to offer certain advantages over T. N. T., namely, low cost, insensitiveness to rifle bullet fire and to friction or impact, ample supply of raw materials, etc.

MANUFACTURE.

Nitrostarch is prepared by treating starch with a mixture of nitric and sulphuric acids, just as nitrocellulose results from similar treatment. It can be prepared from any variety of starch, but it is claimed that cassava or tapioca starch gives a slightly more stable product than ordinary corn starch. The starch must first be freed from impurities such as fats and oils and water-soluble matter, then carefully dried at low temperatures, screened, etc. It is fed slowly into the acid mixture in an iron nitrator provided with suitable agitation and cooling surface, in order to avoid overheating from violent local action. This treatment converts the starch into starch

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nitrate (commonly but incorrectly referred to as nitrostarch), without any change in appearance, but a decided change in chemical properties.

The nitrated product is separated from the excess of spent nitrating acid, drowned in water, washed thoroughly to remove all traces of free acid, then separated from the water in filters or centrifugal wringers, and finally spread out on trays to dry in suitable dry houses heated with warm air to a temperature not exceeding approximately 35° to 40° C. (about 100° F.).

The drying operation, especially the handling of the warm, dry product, is the only really dangerous operation connected with the manufacture, the dry nitrostarch being highly inflammable, capable of being ignited by the slightest spark such as might result from a static charge, and when once ignited, burning with explosive violence.

The mixing of the dry nitrostarch with the "dope" materials, as the inert ingredients of such explosive mixtures are frequently called, is a simple operation, carried out in large revolving mixing barrels. All of the "dope" materials must first be ground to the proper degree of fineness and dried to the proper moisture content, so that the moisture content of the finished explosive will not be in excess of the prescribed amount. Granular nitrostarch explosives, such as "grenite," are usually prepared by spraying the dry material with a solution of the binding material while the mixture is being agitated in a revolving mixer. The resulting granules are dried and screened to proper size.

CHEMICAL AND PHYSICAL PROPERTIES.

Nitrostarch itself is a white, finely divided material, quite similar in appearance to ordinary powdered starch. When observed even under the microscope there is no appreciable difference between nitrated and unnitrated starch until the granules are treated with iodine, which colors the unnitrated starch blue but does not affect the nitrated product.

Nitrostarch is insoluble in water and does not gelatinize or form a paste when heated with water, thereby differing from starch. Its solubility in alcohol and in mixtures of alcohol and ether depends on its percentage of nitrogen or the extent to which it has been nitrated. The grade of nitrostarch ordinarily employed contains from about 12.50 to 12.75 per cent nitrogen; that prescribed for military purposes contains at least 12.80 per cent. All nitrostarch is readily soluble in acetone, the solubility in ether alcohol, in general, increasing as the nitrogen content decreases. It has no great tendency to absorb moisture from the atmosphere beyond the amount of 1 to 2 per cent.

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Trench grenade or trench mortar shell explosive differs greatly in appearance and certain of its properties from straight nitrostarch, being of grayish-black color and of about the consistency of ordinary brown sugar, having a slightly damp feel and tendency to pack under compression, due to the small amount of mineral oil contained as an ingredient. This oil, besides decreasing the sensitiveness of the explosive to ignition and to shock or friction, helps to reduce its attraction for moisture, the mixture of ammonium nitrate and sodium nitrate which it contains being very hygroscopic. In spite of this coating of oil, the Trojan explosive, when spread out in a thin layer in a damp atmosphere, will absorb moisture to such extent that it becomes decidedly wet. Under ordinary working conditions, however, there is no difficulty in loading this explosive and in avoiding the absorption of an undesirable amount of moisture.

Grenite, which is almost entirely pure nitrostarch with the addition of a small amount of oil and a binding material, differs greatly in appearance from Trojan explosive, being in the form of small white, hard granules which run freely without sticking together. Since it contains no ammonium nitrate or other hygroscopic materials, grenite has no particular tendency to absorb moisture even in damp atmospheres.

SENSITIVENESS.

Pure dry nitrostarch is more sensitive to impact than T. N. T. but less sensitive than dry guncotton or nitroglycerin. As mentioned above, it is highly inflammable and readily ignited by the slightest spark such as may result from friction, and, like black powder, burns with explosive violence. It is readily detonated by a mercury fulminate detonator.

Trojan explosive and grenite are both much less sensitive than straight nitrostarch, being required to pass the pendulum friction test of the United States Bureau of Mines and the rifle bullet test, when packed in pasteboard containers. In heavy metal containers these explosives frequently ignite and burn when penetrated by a rifle bullet and in rare instances have exploded under this test.

Trojan explosive is especially insensitive to ignition, being rather difficult to ignite with the flame of a match when spread out unconfined. When once ignited, however, especially in any quantity, it burns fiercely, with a light-colored smoke.

Nitrostarch explosives are readily detonated by mercury fulminate detonators, a No. 6 detonator, containing one grain of fulminate composition, producing complete detonation, unless the explosive has been rendered unduly insensitive by the absorption of excessive moisture or by other cause.

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An important consideration in the case of military explosives, especially those intended for trench warfare purposes, is their sensitiveness to explosion by influence; that is, their tendency to detonate from the shock of a near-by explosion. The Trojan explosive has been found especially insensitive to such effects, as shown by the following tests:

Three malleable iron hand grenades were loaded with Trojan grenade explosive, and packed in a small wooden box divided by means of light wooden partition into three compartments, into each of which a grenade fit snugly in upright position. The two grenades in the end compartments were provided with plugs closing the filling holes and the center grenade with a No. 6 detonator and black powder fuse, the fuse passing out through a small hole in the wooden cover of the box. The center grenade was then detonated by means of the detonator and fuse. On collecting the fragments it was found that, while the center grenade had been broken into hundreds of small fragments indicating normal detonation, the adjacent ones had been merely broken into several large pieces by the force of this explosion, a large part of the powder in them being recovered unconsumed, indicating that only the central grenade had detonated.

In another test, fifteen 3-inch Stokes trench mortar shells were loaded with Trojan explosives, and packed in the usual manner—three in each of five of the regular wooden shipping cases. These cases were placed on end in a row, broad sides in contact, in a pit 5 feet deep, and the pit filled with earth. A fuse and detonator were inserted in the shell farthest removed from the center of this assembly. The detonation of this shell was complete, as indicated by the fragments dug out of the small crater produced. Of the other 14 loaded shell, 9 were recovered uninjured, 1 was broken into several large fragments indicating a low order of explosion, and the remaining 4 were merely split open by the shock of the adjacent explosion, the explosive contained in them having been burned. A similar test of 15 shells loaded with 50/50 amatol resulted in complete detonation of the 15 shells, as indicated by the fact that a very large crater was produced and no unexploded shell or large fragments recovered.

STABILITY.

Early attempts to manufacture nitrostarch resulted in the production of material which was decidedly unstable, and numerous statements found in the literature of explosives refer to nitrostarch as being unsatisfactory for use as an explosive because of sensitiveness and instability. The manufacturers in this country, however, suc-

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ceeded a number of years ago in placing on the market nitrostarch explosives which proved highly satisfactory in these respects and found considerable application as blasting explosives. More recent developments led to a product which entirely met the strict requirements prescribed for military explosives, and there is every reason to believe that the nitrostarch explosives adopted by the Ordnance Department have excellent keeping properties if properly stored in dry atmosphere at reasonable temperatures.

The Trojan explosive, however, if allowed to absorb undue quantities of moisture, especially in a warm atmosphere, may tend to deteriorate owing to gradual decomposition. Such deterioration cannot result in a dangerous condition because it is accompanied by a continual loss of explosive strength and sensitiveness.

EXPLOSIVE PROPERTIES.

Pure nitrostarch detonates, when properly compressed, at a rate of probably at least 20,000 feet per second. In the case of Trojan explosive, containing only about 25 per cent nitrostarch, the rate of detonation is lower but the large gas volume and energy content makes this explosive quite suitable for the purpose, as is indicated by the result of fragmentation tests simulating as nearly as possible service conditions.

In judging the suitability of a grenade explosive from the results of fragmentation tests, consideration is given to the number of fragments of an "effective" size, rather than to the total number of fragments, for the reason that it is considered that the smaller fragments would have an almost negligible effect against personnel. As a result of actual penetration tests it has been concluded that fragments which pass through a screen having two openings to the linear inch and are retained on a screen having four openings to the linear inch can be considered as the most effective and in reporting the results of fragmentation tests these fragments are sometimes designated as "effective" fragments.

Fragmentation results in grenades vary over a considerable range, depending on the exact qualities of the metal. With a charge of approximately 2.5 ounces of Trojan grenade explosive the "effective" fragments will vary from about 100 to 150 and total fragments from 200 to 500. Grenite, being nearly pure nitrostarch, gives greater fragmentation, about 1½ ounces of the explosive giving fragmentation equal to the 2.5 ounce charge of Trojan powder. A charge of 2½ ounces of T. N. T. gives fragmentation only slightly inferior to that of the Trojan powder.

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In general, it may be said that the nitrostarch explosives are approximately equal to T. N. T. or 40 per cent dynamite in explosive strength.

USE, MILITARY AND COMMERCIAL.

The Trojan nitrostarch explosive has been used as the bursting charge for hand grenades, rifle grenades, and Stokes trench mortar shell. It is well adapted to such purposes but has not been considered for use as a bursting charge for high explosive gun shell. Its physical consistency is such that it must be loaded into grenades through the small filling hole, by means of vibrating machines, the explosive being "jarred" into the grenade through small funnel openings. Trench mortar shell are loaded by hand-stemming and have also been loaded with the Trojan explosive by means of a screw-filling machine.

Grenite has been approved only for grenades and is considered too sensitive for use as a trench mortar shell explosive. Being granular and "free-running" it is readily loaded into the grenades through funnel openings, no attempt being made to pack it to a high density.

Nitrostarch has been considered for the manufacture of smokeless propellant powder, and numerous attempts have been made to develop a satisfactory powder of this type, but the problem can not as yet be considered solved.

Nitrostarch explosives similar to Trojan grenade explosive have been used for a considerable number of years as blasting explosives for use in mining, quarrying, and other engineering operations, and have met with considerable success as substitutes for the more expensive nitroglycerin explosives. Among the numerous advantages of nitrostarch explosives may be noted the fact that, unlike nitroglycerin explosives, they are nonfreezing.

CARE IN STORAGE AND HANDLING.

The storage of nitrostarch explosives in general is mainly a fire risk. That is to say, the danger accompanying storage is more one of fire than of explosion. Burning may, however, proceed at such rate as to be almost explosive in nature, and the fact that nitrostarch can be exploded by impact must not be overlooked.

Storage magazines must be kept at as low temperatures as possible in order to avoid as much as possible the tendency of nitrostarch to undergo decomposition on heating. A reasonably dry atmosphere in magazines is also highly essential, as Trojan explosive especially, on account of its ammonium nitrate content, has a considerable affinity for moisture.

There is no danger of poisoning of any kind connected with the handling of nitrostarch explosives.

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INSPECTION.

Specifications.—The chemical composition of Trojan explosive as prescribed by Ordnance Department specifications is as follows:

	Not less than—	Not more than—
	Per cent.	*Per cent.*
Nitrostarch	23.0	27.0
Ammonium nitrate	31.0	35.0
Sodium nitrate	36.0	40.0
Charcoal	1.5	2.5
Heavy hydrocarbons	.5	1.5
Antiacid	.5	1.5
Diphenylamine	.2	.4
Moisture		1.2

The chemical composition of grenite is prescribed as follows:

	Not less than—	Not more than—
	Per cent.	*Per cent.*
Nitrostarch	95.5	98.25
Petroleum oil	.75	2.00
Gum arabic	.75	2.00
Moisture		1.00

METHODS OF ANALYSIS.

The Ordnance Department specifications prescribe the following method for the analysis of Trojan explosive:

(*a*) Moisture: Approximately 5 grams of the sample, accurately weighed out, shall be spread evenly on a 90 mm. watch glass (3½ inches diameter) and placed in a desiccator over concentrated sulphuric acid. Loss in weight after 48 hours is taken as moisture. As an alternative method, a vacuum desiccator may be used with sulphuric acid (specific gravity, 1.84) as a desiccating agent and employing a vacuum of at least 700 mm. of mercury. After 24 hours the vacuum shall be slowly relieved and the loss in weight taken as moisture. The percentage of moisture shall not exceed 1.2 per cent.

(*b*) Ether extract: Approximately 10 grams of the sample are accurately weighed out and placed in a porous crucible (Gooch crucible, with thin asbestos mat, or an alundum filtering crucible) and extracted with pure petroleum ether of 0.640 to 0.660 specific gravity. After complete extraction, the crucible and contents are dried by means of a stream of dry air until complete removal of the petroleum ether, after which the crucible shall be placed in a steam oven and dried to constant weight at approximately 70° C. The difference in weight between the original weight of the sample, after deducting weight of moisture, and the weight after extraction is taken as the heavy hydrocarbon oil present, together with the diphenylamine. The diphenylamine in this mixture may be determined by means of the Dumas method for determining nitrogen.

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(*c*) Water extract: The material in the crucible after removal of the heavy oil consists of nitrostarch, ammonium nitrate, sodium nitrate, charcoal, and sodium bicarbonate. By treatment with warm distilled water, the ammonium nitrate, sodium nitrate, and sodium bicarbonate are removed, and the material in the crucible after drying at 80° C. for several hours consists of nitrostarch and charcoal. The loss in weight in the water extraction is determined and also the weight of the crucible plus nitrostarch and charcoal. These two factors are then used in the subsequent calculations.

(*d*) Sodium bicarbonate: The water extract is made up to a fixed volume. One portion is taken for the determination of the sodium bicarbonate present. This is determined by titration with N/10 sulphuric acid, using methyl orange as an indicator, and the alkalinity so found is calculated to sodium bicarbonate.

(*e*) Ammonium nitrate: At the option of the inspector, the percentage of ammonium nitrate is determined by taking an aliquot portion of the water extract, adding caustic soda until the solution is strongly alkaline, and then distilling in an apparatus as used for ammonia determinations and collecting the distillate in a known volume of standard sulphuric acid. The excess acid is titrated with standard alkali, methyl orange being used as an indicator, and the result is then calculated to ammonium nitrate.

(f) Sodium nitrate: An aliquot part of the water extract is acidified with nitric acid and the solution evaporated to dryness in a platinum dish. It is then ignited at a low red heat over a suitable flame, using care to avoid loss of the contents. The weight is then taken and a correction made for the amount of sodium bicarbonate present and the results regarded as sodium nitrate present. Following this procedure, the ammonium nitrate would be taken by difference, in order to avoid the determination of ammonia.

(*g*) Charcoal: The residue in the crucible after the water extraction consists of nitrostarch and charcoal. This material is best extracted in a Wiley extractor with warm acetone until no further soluble material is obtained. The crucible is then dried in a stream of dry air and further dried for several hours at 100° C. The weight of the charcoal is taken as the increase in weight of the crucible over its original weight empty.

(*h*) Nitrostarch: The difference between the sum of nitrostarch and charcoal content as determined in paragraph (*c*), and the percentage of charcoal as found by paragraph (*g*), represents the nitrostarch present.

The analysis of grenite is carried out in a similar manner, the ether extraction removing the oil, the water extraction dissolving the gum arabic and leaving the nitrostarch.

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CHAPTER XI.

TETRYL.

The high explosive commonly known as tetryl (sometimes as tetralite or pyronite) is designated by the chemist as tri-nitro-phenyl-methyl-nitramine and also frequently improperly called tetra-nitro-methyl-aniline. It is closely related to T. N. A. (tetra-nitroaniline), resembles it in many of its properties, and is used for similar purposes.

MANUFACTURE.

Tetryl is a derivative of benzene and is therefore in the same class of aromatic nitrocompounds as T. N. T. and T. N. A. Although the explosive manufacturer usually starts with dimethylaniline as his raw material, the entire process, beginning with benzene, is indicated as follows: Benzene is nitrated to nitrobenzene by means of a mixture of nitric and sulphuric acids and the resulting nitrobenzene reduced with iron filings and hydrochloric (muriatic) acid to aniline. Aniline is then combined with methyl alcohol (wood alcohol) by heating these ingredients under pressure in the presence of sulphuric acid or iodine, yielding dimethylaniline.

The dimethylaniline is a yellowish oily liquid of slightly lower specific gravity than water. Prior to nitrating it is dissolved in a large excess of 98 per cent sulphuric acid because if treated direct with mixed acid a very violent reaction results. This solution in sulphuric acid is now added to the mixture of nitric and sulphuric acids in a nitrator provided with means for cooling and agitation. The mixing is carried on very slowly in order to avoid overheating and possible explosion.

The tetryl separates out from the acid mixture and is freed from the acid by filtration and washing with water, after which it is dried in a current of warm air until its moisture content is not more than 0.05 per cent.

CHEMICAL AND PHYSICAL PROPERTIES.

Tetryl is a fine crystalline powder of a yellow color, practically insoluble in water, but soluble in acetone, benzene and other solvents. It is readily recrystallized and can therefore be obtained in very pure condition if desired. It melts, when pure, between 129° and 130° C. Tetryl is poisonous when taken internally, and precaution is neces-

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sary in its manufacture, especially as regards the dust encountered in handling and packing the dry material. With the exception of T. N. A., it has a higher nitrogen content (24.4 per cent) than any other military explosive.

STABILITY AND SENSITIVENESS.

Tetryl is stable at all temperatures which may be met with in storage. When heated above its melting point it undergoes gradual decomposition and explodes at about 186° C. (335° F.). It is more sensitive to shock or friction than T. N. A., being of about the same order of sensitiveness as picric acid. It is more sensitive to detonation by means of mercury fulminate than is T. N. T., resembling T. N. A. in this respect. Like T. N. A., it is also readily exploded by the penetration of a rifle bullet.

Unlike T. N. A., tetryl does not undergo decomposition when heated with water at temperatures somewhat higher than ordinary storage temperatures.

EXPLOSIVE PROPERTIES.

Tetryl has been found to have a rate of detonation of about 24,000 feet per second—practically the maximum rate obtained with T. N. T. Strength tests, such as the Trauzl lead block test, show tetryl to be stronger than any other military high explosive, the average expansion produced in the lead block for the more common high explosives being as follows:

T. N. A., 380 cubic centimeters.
Tetryl, 320 cubic centimeters.
Picric acid, 300 cubic centimeters.
T. N. T., 260 cubic centimeters.

USE, MILITARY AND COMMERCIAL.

The high explosive strength and quickness (or "brisance") of tetryl would seem to adapt it for use as a bursting charge, but its sensitiveness to mechanical shock is such that if used as a shell filler it would not withstand the shock of discharge of the gun. It is, however, sufficiently insensitive so that when highly compressed into a booster it is perfectly safe. In this condition it is readily detonated by the charge of mercury fulminate in the fuze of the shell, and the violence of its detonation insures a high order of detonation of the bursting charge.

Tetryl is therefore generally adopted in this country as a booster explosive either alone or combined with T. N. T. (Grade I), the two explosives being usually loaded separately into the booster casing, in

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the form of highly compressed pellets perforated with a central hole of suitable size for the detonator of the fuze.

It is also used in detonators for both military and commercial purposes, as a partial substitute for the mercury-fulminate charge, the tetryl being pressed into the bottom of the detonator shell, covered with a small priming charge of fulminate and the entire charge partly confined by a perforated inner capsule of copper.

PRECAUTIONS TO BE OBSERVED IN HANDLING AND STORAGE.

The same precautions should be observed in the handling and storage of tetryl as in the case of other sensitive high explosives. It should be kept dry because moisture interferes with its effectiveness. It must be properly protected from bullet fire in brick or hollow tile magazines with iron doors and window shutters. Detonators, blasting caps, fuzes, dynamite, etc., must not be stored with tetryl. Rubber-soled shoes should be worn in magazines and every precaution taken to prevent ignition or explosion from friction or blows due to rough handling.

INSPECTION.

Specifications.—Ordnance Department specifications require that tetryl shall have the following properties:

(*a*) Melting point—not less than 128° C.

(*b*) Acidity—not more than 0.01 per cent (as H_2SO_4).

(*c*) Insoluble in acetone—not more than 0.30 per cent.

(*d*) Ash—not more than 0.15 per cent.

(*e*) Moisture and other volatile matter—not more than 0.05 per cent.

(*f*) Sodium salts—not more than trace.

(*g*) Color—light yellow.

(*h*) Fineness—12-mesh (screen openings 0.058 of an inch, wire 0.025 of an inch).

Methods of testing—The prescribed methods of testing tetryl for acceptance are as follows:

Melting point: Fifteen grams of tetryl which have been dried 24 hours in a vacuum desiccator over calcium chloride are ground in a mortar to pass a 40-mesh screen and quartered. A quarter is ground to pass a 100-mesh screen, the latter material being used in the test. The capillary tubes used for making the test must be of uniformly fine bore. A standardized thermometer shall be used and corrections made for emergent stem. In charging the capillary, the tube should be filled to approximately one-fourth inch from the bottom and the material in the capillary placed opposite the center of the bulb of the thermometer. Efficient agitation must be provided for

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the bath, and the temperature of the bath raised rapidly until approximately 120° C. From this point the rate of heating is adjusted so that the temperature increases at the rate of not more than 1° in 3 minutes. The melting point shall be taken at the appearance of the first meniscus across the tube.

Acidity: A known weight of the ground sample, approximately 10 grams, is shaken for 5 minutes in 50 c. c. of boiled distilled water. The solution is then filtered and washed with not more than 50 c. c. of boiled distilled water. The filtrate is titrated with N/50 sodium hydroxide solution, using phenolphthalein as an indicator and results calculated as sulphuric acid.

Insoluble matter: A known weight, approximately 10 grams of the sample, is dissolved in 75 c. c. of acetone and filtered through a tared Gooch. The residue in the crucible is washed with not less than 25 c. c. of acetone and dried for 4 hours at 100° C. and weighed.

Ash: The dried Gooch crucible, containing the residue insoluble in acetone, is carefully ignited, cooled in a desiccator and weighed.

Moisture and volatile: A known weight, approximately 10 grams of the sample, is dried in a shallow glass jar or dish for 24 hours over sulphuric acid and then weighed. The material should be thinly spread, in no place being over 0.5 cm. in height. The jar or dish is covered with an air-tight cover during all weighings.

Sodium salts: Ten grams dry tetryl are boiled in 50 c. c. of distilled water, cooled, filtered, and the filtrate acidified with acetic acid and evaporated to a 10 c. c. volume, cooled and filtered. The filtrate is made alkaline with ammonium hydroxide and 5 c. c. of a 10 per cent solution of ammoniacal copper sulphate added. No crystals of cupro ammonium picrate shall be separated after five minutes' standing.

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CHAPTER XII.

TETRANITROANILINE (T. N. A.).

Tetranitroaniline, commonly known by the abbreviation T. N. A., is a high explosive derived from benzene, the process of manufacture and use of which in this country is patented by Dr. B. J. Flurscheim, an English chemist, under United States Patents Nos. 1,045,011 and 1,045,012, November 19, 1912, and No. 1,074,545, September 30, 1913.

MANUFACTURE.

It is manufactured by a rather complicated process, beginning with benzene as a raw material. Benzene is first nitrated by means of a mixture of nitric acid and sulphuric acid to dinitrobenzene (D. N. B.), which, in turn, is converted by treatment with a solution of sodium sulphide to metanitraniline (M. N. A.); the metanitraniline, on treatment with sulphuric acid, is converted to metanitraniline sulphate (M. N. A. S.), which is finally nitrated by means of a mixture of strong nitric and sulphuric acids to tetranitroaniline (T. N. A.). In this final nitration, the M. N. A. S. is dissolved in a large excess of strong sulphuric acid, and a mixed acid added with stirring and cooling. The finely crystalline T. N. A. separates out from the acid mixture as the reaction proceeds, and is finally recovered by filtration, washed thoroughly with water to remove all free acid, filtered again from the water and finally dried in a current of air at a low temperature.

CHEMICAL PROPERTIES.

T. N. A. is generally admitted to be practically the strongest of all solid high explosives. It is a finely crystalline material varying in color from greenish yellow to olive green, the fine crystals, which appear under the miscroscope as square plates, being small enough to pass through a sieve of about 80 mesh to the linear inch. Owing to the fact that it has no tendency to absorb moisture from the atmosphere, it does not cake in containers.

When dry, T. N. A. is not in the least affected by exposure for considerable periods to temperatures as high as even 75° C.; in fact, such treatment improves its apparent stability as indicated by the usual "heat test" with potassium iodide—starch paper—for the reason that such heating probably eliminates traces of acid impurities. When moist, however, heating at temperatures as low as 50°

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C. (122° F.) will cause a very gradual decomposition of T. N. A., which, however, is not of a dangerous nature, but probably only results in a loss of explosive strength. Traces of acid decomposition products are liberated by such treatment.

T. N. A. when properly manufactured and thoroughly dried passes satisfactorily all of the usual tests for stability, including the 65.5° C. heat test and the 135° C. test.

Like T. N. T., T. N. A. has no action on metals with which it may be in contact, differing in this respect from picric acid, which tends to form metallic salts with almost all metals.

T. N. A. is practically insoluble in water, but readily soluble in acetone. It melts only at a temperature of about 210° to 215° C., and then only with decomposition. On heating rapidly to higher temperatures it undergoes rapid decomposition or deflagration with flame, but does not detonate. It contains a higher percentage of nitrogen than any of the well-known military explosives—25.6 per cent, as compared with 24.4 per cent for tetryl, 18.5 per cent for T. N. T., and 18.3 per cent for picric acid.

TOXIC PROPERTIES.

Although the manufacture of T. N. A. involves the preparation of intermediate products which are of a poisonous nature, such as dinitrobenzene and metanitroaniline, T. N. A. itself is not poisonous. This has been demonstrated by experimentation in which T. N. A. was administered internally to small animals with no bad results. In contact with the skin it produces yellow stains, similar to that resulting from picric acid, but no poisoning results from this.

SENSITIVENESS TO HEAT, SHOCK, AND DETONATION.

Mention has already been made of the fact that T. N. A. melts only at very high temperatures (210° to 215° C.) and then only with decomposition. It is therefore obvious that this explosive, unlike T. N. T., is never used in cast form, but always in its original crystalline condition or highly compressed.

T. N. A. is, in general, more sensitive to the shock of blows or friction than is T. N. T., although the difference in the sensitiveness of these two explosives is not great. For example, in one series of tests it was found that T. N. T. detonated under a 200-kilogram (about 440 pounds) drop weight with a fall of 120 centimeters (48 inches), while under the same conditions T. N. A. detonated under the effect of a drop of 100 centimeters (40 inches). It is to be noted, however, that the detonation produced in T. N. A. by such means invariably spreads through the entire quantity of explosive, while with T. N. T.

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detonation is communicated with such difficulty that usually only a portion of the explosive detonates.

The effect of penetration of a rifle bullet serves to show a striking difference in the sensitiveness of T. N. T. and T. N. A. Bullets fired from a service rifle into a box of T. N. T. at a range of about 100 feet show no effect whatever, while, under similar conditions, T. N. A. detonates with great violence.

T. N. A. is more sensitive to the effect of detonators than is T. N. T. Under certain conditions a confined charge of T. N. T. was found to require 0.26 gram of mercury fulminate to produce complete detonation, while a similar charge of T. N. A. required only 0.20 gram of fulminate. Under general conditions of use, T. N. A. invariably detonates readily and completely with a No. 6 detonator (containing 1 gram or 15.4 grains of mercury fulminate or its equivalent).

Even when moistened with as much as 6 per cent of water, T. N. A. detonates completely with a No. 6 detonator, and with 16 per cent water detonation was obtained with a No. 6 detonator and a small priming charge of dry T. N. A.

EXPLOSIVE PROPERTIES.

No data is available at present as to the rate at which T. N. A. detonates, but it is undoubtedly very high, probably at least 25,000 feet per second. The explosive strength is, however, indicated by other tests, such as the Trauzl lead block test, which measures the expansion produced in a cylindrical hole in a cast lead cylinder about 8 by 8 inches, by the explosion of 10 grams (about $\frac{1}{3}$ ounce) of the explosive. In this test it has been found that T. N. A. gives an expansion of about 380 cubic centimeters, as compared with the following approximate results on other high explosives: Tetryl 320 c. c., picric acid 300 c. c., T. N. T. 260 c. c. On the basis of this comparison T. N. A. may be regarded as at least 40 per cent stronger than T. N. T.

USE.

T. N. A. is considerably more expensive to manufacture than T. N. T., and for this reason, as well as because of its greater sensitiveness to shock, it is not considered suitable for use as a bursting charge for high explosive shell, drop bombs, etc. Its sensitiveness is greatly reduced by the addition of as little as 5 per cent of paraffin, or of 25 per cent of dinitrobenzene, and such mixtures have been loaded in shell and fired through armor plate without explosion. Such additions to T. N. A. necessarily cause a reduction in explosive strength, and these mixtures have therefore not been adopted for use as shell explosives.

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The high cost of T. N. A. constitutes a drawback to the commercial as well as the military use of T. N. A. It has, however, been successfully used as an ingredient of cheap, relatively insensitive blasting explosives, for the purpose of increasing both strength and sensitiveness to detonation. It has also been used to advantage as a partial substitute for mercury fulminate in commercial blasting caps or electric detonators, where it has the advantage that it can be compressed to very high densities without losing its sensitiveness to detonation under the influence of a small priming charge of fulminate.

PRECAUTIONS TO BE OBSERVED IN HANDLING AND STORAGE.

Because of the fact that in the presence of moisture T. N. A. undergoes a gradual decomposition even at relatively low temperatures, it is important that it be kept dry in storage. Efficient ventilation in the magazine is of great assistance in avoiding dampness.

The fact that T. N. A. is readily detonated by the effect of rifle bullets makes it highly important that it be stored only in bullet-proof magazines. Hollow tile construction has been found to be bullet proof. Magazines of lighter type containing T. N. A. should be protected by barricades. Exposed doors and window shutters should be of heavy iron.

It must be remembered that T. N. A. can be exploded by friction or blows of sufficient force and proper care should be taken to avoid unduly rough handling. The wearing of rubber-soled shoes in magazines is advisable.

Detonators, blasting caps, dynamite or similar highly sensitive explosives, must not be stored in the same magazine with T. N. A.

INSPECTION.

The specifications covering the chemical requirements for T. N. A., together with the methods for testing, are as follows:

Nitrogen content: Nitrogen content shall be not less than 25.25 per cent when tested by the Dumas method.

Melting point: Melting point shall be not less than 208° C. when heated in a capillary tube with a temperature increase of 5° C. per minute.

Insoluble in acetone: The percentage of material in the sample which is insoluble in C. P. acetone shall not exceed 0.75 per cent when tested as follows: Five grams of the material are thoroughly extracted with C. P. acetone in a filtering crucible and the residue dried to constant weight at 95° to 100° C.

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Moisture: The material shall contain not more than 0.30 per cent of moisture when tested as follows: Weigh out 10 grams of the sample onto a 3-inch watch glass and dry in an oven at 95° to 100° C. for one hour.

Acidity: The acidity shall not exceed 0.05 per cent when tested as follows: Weigh out 10 grams of the sample into a stoppered bottle of approximately 250 cubic centimeters capacity, add 150 cubic centimeters of neutral distilled water, and allow to stand at room temperature with frequent shaking for 30 minutes.. Filter off the water and wash the residue with two successive 20 cubic centimeter portions of cool neutral distilled water, adding the washings to preceding filtrate. Titrate filtrate with N/50 NaOH solution, using 15 drops of 0.5 per cent phenolphthalein solution as indicator.

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CHAPTER XIII.

MERCURY FULMINATE.

Mercury fulminate is the explosive most commonly used for bringing about the detonation of high explosives. It detonates completely and with great violence on mere ignition by means of a flame such as the spit from a fuse or by means of an electrically heated wire. This fact, together with its property of starting the detonation of other explosives, makes it a most suitable detonator material.

MANUFACTURE.

It is prepared, generally on a relatively small scale, by the action of alcohol on mercury nitrate in nitric acid solution. The raw materials required are, therefore, only metallic mercury, nitric acid, and ethyl alcohol (common grain alcohol of 95 per cent strength). All of these materials must be of high purity, in order to produce a satisfactory product. The process of manufacture is quite simple and may be carried out as follows:

About 1 pound of pure mercury is weighed carefully, added to a weighed charge of from 8 to 10 pounds of strong nitric acid in a suitable bottle or acid pitcher, and allowed to stand until completely dissolved, giving a solution of mercury nitrate in the excess of nitric acid. A large number of such charges are usually prepared and allowed to stand over night until dissolved.

The acid solution of mercury is then poured into about 8 to 10 pounds of 95 per cent alcohol which has previously been measured into a large thin glass flask or balloon of about 10-gallon capacity supported in a suitable rack under an open shed or in the open air. A violent reaction results, usually within two or three minutes, the mixture in the balloons appearing to be boiling violently as a result of the evolution of great quantities of vapors and fumes. These vapors, at first white, become brownish red in color toward the end of the reaction, as the heat generated drives off nitric acid. At this point a small amount of dilute alcohol is usually added to prevent excessive heating, which would decompose the mercury fulminate produced. The reaction usually lasts about one hour, when the fuming ceases and the liquid remaining in the balloon is found to contain the crystalline fulminate.

In some plants the balloons are placed in troughs of water in order to control the temperature, and the necks of the balloons are con-

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nected with a suitable condenser system where the alcohol driven off in the fumes is recovered.

After cooling, the charge in the balloons is dumped onto a cloth screen and washed with cold running water until all free acid is removed and the fine impurities in the form of "fulminate mud" washed away. The washed fulminate is then drained and packed in cloth bags, which are usually stored in crocks of water in vaults, or in underground concrete tanks of water, until required for use. For shipment, the bags are packed in barrels of wet sawdust.

When required for use, the fulminate is removed from the bags, the water drained off, and the wet fulminate spread on cloth to dry in dry houses carefully regulated at a temperature of about 110° F. One pound of mercury produces approximately 1¼ pounds of dry mercury fulminate.

CHEMICAL AND PHYSICAL PROPERTIES.

Mercury fulminate is a heavy, crystalline solid, white when pure, but ordinarily of a faint brownish yellow or grayish tint. It has practically no tendency to absorb moisture from the atmosphere. It is only slightly soluble in water, 100 parts of water at 60° F. dissolving less than 0.01 part of fulminate, and may be kept in contact with water for long periods of time without undergoing change.

The size of the crystals of mercury fulminate is an important factor, since it has been determined that very finely divided fulminate, consisting mostly of fragments of crystals and usually containing an excessive amount of impurities, is less efficient in detonating value and strength than larger crystals. In specifying the size of crystals desired, however, consideration has been given to the possibilities of controlling this feature in manufacture and also to the fact that there is some reason to believe that very large crystals of fulminate are more sensitive to friction or shock than smaller ones. Ordnance Department specifications prescribe that at least 70 per cent of the crystals shall be within the limits of 0.25 to 0.60 millimeters in length and 0.15 to 0.35 millimeters in diameter. This determination is readily made under the microscope.

IMPURITIES.

Mercury fulminate is required by Ordnance Department specifications to be at least 98 per cent pure and the amounts of impurities which it may contain are strictly limited. The most objectionable impurities are (1) free metallic mercury, for the reason that it readily attacks the copper or brass with which it may be in contact when loaded into fuzes, detonators, or primers, causing the

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metal to become brittle; (2) acidity, which would cause deterioration of the explosive composition and corrosion of metal parts; (3) insoluble material, such as sand and grit, which might cause explosion of the dry fulminate in the loading operations. If improperly manufactured or incompletely washed, the fulminate may also contain various compounds of mercury which might produce decomposition and would certainly diminish the explosive efficiency of the fulminate.

ACTION ON METALS.

Dry mercury fulminate has very little tendency to react with metals at ordinary temperature, although to avoid the amalgamating effect of any small amounts of free mercury present, the brass or copper of the containers is usually varnished or lacquered. Wet mercury fulminate, however, reacts with certain metals, especially brass, with much greater readiness.

STABILITY AND SENSITIVENESS.

Mercury fulminate has been kept for long periods both dry and wet, and is believed to undergo practically no change when properly manufactured and stored. It is never stored in quantity in the dry condition except when loaded into detonators, fuzes, or primers, for the reason that when dry, it is readily detonated by friction or shock. Whereas, the great majority of high explosives will burn without detonating when ignited by a flame, especially if a relatively small amount of the explosive is ignited, mercury fulminate is one of the so-called "primary" or "initiating" explosives which detonate completely on being heated to their ignition point by means of a flame or hot wire, thereby becoming suitable for use as detonators for other less sensitive explosives.

The presence of even small amounts of moisture in mercury fulminate greatly reduces its efficiency, and as little as 1 per cent is said to cause failure to detonate. Fulminate completely saturated with water may, however, be detonated by the detonation of dry fulminate in contact with it.

By the usual methods of determining ignition temperature, mercury fulminate detonates at a temperature of about 100° C. (about 356° F.), but under varying conditions detonation may result at much lower temperatures. The sensitiveness to shock is much greater at elevated temperatures than under storage conditions.

When loaded into commercial detonators, mercury fulminate is usually compressed at pressures of about 2,000 or 3,000 pounds per square inch. In this condition its explosive properties are not appreciably different from those of loosely compressed material. At

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greater densities obtained by higher pressures, there is a gradual reduction in strength, until at such extreme pressures as 75,000 pounds per square inch fulminate entirely loses its property of detonating and will only burn. In this condition it is referred to as "dead pressed."

Although fulminate can be pressed under very high pressures without explosion, the presence of any particles of sand or grit is very dangerous in any pressing operation. Presses for loading are always carefully protected by heavy barricades, and no one is permitted to be near the press during operation.

The readiness with which dry mercury fulminate detonates from the effect of blows or friction is the chief reason for the fact that its transportation and storage in the dry state is not permitted. Tests with a special type of impact machine showed that mercury fulminate detonated from the blow of the falling weight dropped from a height of only two centimeters (about 0.8 inch), while T. N. T. in the same apparatus required a drop of about 120 centimeters (48 inches).

EXPLOSIVE PROPERTIES.

The efficiency of mercury fulminate as a detonator for other explosives can not be judged by its behavior when submitted to the usual tests for high explosives. For example, it has been found by the usual methods that mercury fulminate has a rate of detonation of only about 12,700 feet per second, as compared with the nearly double rate for T. N. T. under proper conditions. In the Trauzl lead block test, mercury fulminate produces an expansion of only 213 cubic centimeters, T. N. T. giving about 260 cubic centimeters.

The results of many investigations have led to numerous theories for explaining the unique properties of detonators such as mercury fulminate, the general conclusion being that its ability to detonate other explosives is due to the rapid development of a very high initial rate of detonation which subjects the adjacent mass of explosive to a severe shock or blow, "upsetting" its condition of equilibrium, this effect being rapidly transmitted throughout the explosive by a sort of wave action which results in complete detonation at a high rate.

USE.

Mercury fulminate is used only for the purpose of bringing about the detonation of other high explosives or the explosion of propellant explosives. In detonators for commercial or military use it may be used alone but is generally mixed with from 10 to 20 per cent of potassium chlorate, whereby greater efficiency is obtained. Most of the commercial detonators or blasting caps and many of those used

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for military purposes are now composed mainly of tetryl or some similar high explosive combined with a smaller priming charge of fulminate. The usual grades of detonators contain from 15 to 30 grains of fulminate or its equivalent.

The explosion of propellant explosives, as, for example, the smokeless or black powder in small arms cartridges, is effected by the flame from a primer or cap, the charge of which is usually a composition containing mercury fulminate mixed with other flame-producing materials such as potassium chlorate with sulphur or antimony sulphide. The primer is exploded by the impact of the firing pin.

PRECAUTIONS TO BE OBSERVED IN HANDLING AND STORAGE.

Mercury fulminate is always stored thoroughly saturated with water. It is not advisable to store it for any great length of time in the shipping barrels where the bags of wet fulminate are in contact with wet sawdust, for the reason that soluble materials extracted from the sawdust may cause deterioration of the fulminate. The bags should be removed from the barrels and stored in tanks which are kept continually full of water and properly protected from sand or grit which might penetrate the bags and contaminate the fulminate.

When left in the barrels during storage, regular inspection must be made to insure that the barrels are kept always full of water and are not leaking.

Fulminate must not be stored with any other explosives, for the reason that the explosion of even a relatively small amount of dry fulminate may cause detonation of the wet materials, the effect of which might be to detonate any other high explosives in the vicinity.

In case of breakage or other cause by which wet fulminate may be spilled on the floor, it should not be allowed to dry out before cleaning up. Dry fulminate is very sensitive to friction and must be handled with extreme care.

METHODS OF ANALYSIS.

The chemical requirements and methods for analysis of mercury fulminate as prescribed by the Ordnance Department are as follows:

It shall (*a*) be free from acid, (*b*) contain not more than 2 per cent insoluble, (*c*) contain not more than 1 per cent free mercury, (*d*) contain not more than 0.05 per cent chlorine, and (*e*) be at least 98 per cent pure mercury fulminate.

Acidity: When a 10-gram sample of the thoroughly dried materials is placed in a porcelain Gooch crucible having on its bottom a filter paper disk, and washed with two successive 25 cubic centimeter portions of boiled distilled water, the filtrate so obtained shall show

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no red tinge upon the addition of 3 drops of methyl orange solution made up by dissolving one-tenth gram pure methyl orange in 100 cubic centimeters of distilled water.

Insoluble matter: A 2-gram sample of the dry material is dissolved in hot 20 per cent thiosulphate solution, filtered through a tared Gooch. The thio solution is washed out with distilled water, alcohol, and ether, and the Gooch dried at 60° to 70° C., weighed, and insoluble matter calculated.

Free mercury: The dried fulminate of mercury shall not contain over 1 per cent of free mercury when tested as follows:

Treat the residue in the Gooch crucible used for determining the insoluble content of the mercury fulminate with 3 grams of potassium iodide and 6 grams of sodium thiosulphate dissolved in 50 cubic centimeters of distilled water.

The solution is decanted through the Gooch crucible used in determining the insoluble content of the mercury fulminate, and the crucible washed thoroughly with distilled water and dried at 80° to 90° C. for one hour and weighed. The increase in weight of the Gooch crucible is taken as the mercury content of the original 2-gram sample tested and the percentage so determined.

The potassium iodide converts the organic mercury compounds into mercury iodide, which is then soluble in sodium thiosulphate solution. The metallic mercury, not being soluble in potassium iodide and sodium thiosulphate solution, remains behind as a residue in the Gooch crucible, and can therefore be accurately determined.

Mercury fulminate content: Weigh out exactly three-tenths of a gram of the thoroughly dried material that is to be tested and place it in a wide-mouthed Erlenmeyer flask containing approximately 250 cubic centimeters of distilled water.

Then add quickly 30 cubic centimeters of a 20 per cent solution of sodium thiosulphate that has been freshly filtered to remove any precipitated sulphur. The sodium thiosulphate used shall be the very best grade obtainable.

The mixture is shaken for exactly one minute and then at once titrated with N/10 hydrochloric acid, using 3 drops of standard methyl orange solution as indicator.

Begin to titrate exactly one minute after the addition of the sodium thiosulphate. The bulk of the acid should be added immediately and the total time consumed in titration should not exceed one minute.

The per cent of mercury fulminate is calculated from the amount of standard acid used after deducting the amount of N/10 hydrochloric acid required to obtain the same end point on a blank determination.

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Four hydrochloric acid molecules are equivalent to one mercury fulminate molecule, and therefore 1 cubic centimeter of N/10 hydrochloric acid is equivalent to 0.00711575 gram of mercury fulminate.

Chlorides: A 5-gram sample of the thoroughly dried material is placed in a porcelain Gooch crucible having in its bottom a filter paper disk and washed with two successive 25 cubic centimeter portions of distilled water having a temperature between 90° C. and 100° C. To the filtrate, which is most conveniently caught in a test tube, add 3 drops of pure nitric acid having a specific gravity of approximately 1.40 and 10 drops of a 10 per cent solution of silver nitrate made by dissolving 10 grams pure silver nitrate in 90 cubic centimeters of water. If decided turbidity shall appear, rendering decision doubtful, make quantitative test; chlorine shall not exceed 0.05 per cent.

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CHAPTER XIV.

AMATOL.

GENERAL.

Amatol is a mixture of ammonium nitrate and T. N. T. Due to the shortage of toluol during the early stages of the war with Germany, the British Government developed this explosive and adopted it after exhaustive tests as a bursting charge for high explosive shells. The United States Government shortly after its entrance into the war and for similar reasons authorized its use as follows: 50/50 for shells for 75 mm. up to and including 4.7 inches; 80/20 for shells from 4.7 inches up to and including 9.2 inches. The ingredients are mixed by weight. The first figure refers to ammonium nitrate, the second to T. N. T.

PROPERTIES.

Amatol is hygroscopic, insensitive to blows or friction, yet can be detonated by severe impact, has no tendency to form dangerous compounds with metal other than copper or tin, is more insensitive to explosion by influence than T. N. T., and has approximately the same rate of detonation and strength as T. N. T.

MANUFACTURE OR METHOD OF MIXING.

The T. N. T. is melted and incorporated with the ammonium nitrate in a jacketed mixer for a length of time sufficient to insure each grain of the ammonium nitrate being thoroughly coated with the T. N. T. The 50/50 mixture is sufficiently fluid to admit of its being poured or cast. The 80/20 mixture is plastic, resembling moist brown sugar, and must be loaded into the shell by tamping or screw filling.

ANALYSIS.

Raw materials.—The ammonium nitrate and T. N. T. used in the preparation of amatol must conform to Ordnance Department specifications governing these materials, as impurities in both have harmful effects on the resulting product. Oily impurities in the T. N. T. will cause exudation or leakage, while impurities in ammonium nitrate, such as pyridine, cyanide, etc., will cause formation of gas or frothing, resulting in probable cavitation in the shell. Methods

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of analysis for governing the inspection of these materials are given elsewhere in this book.

Sampling.—Samples should be taken from the mixer while the stirrers are rotated, as the T. N. T. and ammonium nitrate have a tendency to segregate. It is desirable to take the sample in an aluminum or thin sheet-iron vessel, a circular piece of stout cardboard being placed in the bottom. To obtain concordant results with duplicate analyses, experience will show that extreme care must be taken with the samples.

Moisture.—Dish and dome method: Heat an aluminum dish and dome (cover) for 15 minutes, cool in the desiccator and weigh. Add approximately 5 grams of the sample and place on the top of a water oven for 3 hours. Cool in a desiccator for 20 minutes and weigh. Loss in weight equals moisture present in the original sample. A small quantity of T. N. T. sublimes but condenses on the inside of the cover, which should be cleaned thoroughly before using in another test.

T. N. T.—Extraction with benzene: Fold a dry filter paper so as to leave a small cavity in the center and weigh in a tared weighing bottle. Place about 2 grams of powdered amatol in the filter paper without removing it from the bottle and reweigh. Transfer the paper and amatol to a small funnel and wash with approximately 75 c. c. hot benzene, adding enough at a time to cover the powder. After about one-half of the benzene has been added the remainder can be poured in rapidly, taking care to wash the sides of the filter paper thoroughly. Transfer the filter paper and residue from the funnel to the top of a steam oven in order to remove the greater portion of the benzene and dry in a tared weighing bottle for one hour. Loss in weight equals T. N. T. plus moisture.

Ammonium nitrate.—Extraction with water: A known weight, approximately 2 grams, is extracted with 50 c. c. warm water, temperature not less than 85° C. After cooling, the solution is filtered and the process repeated three times with 50 c. c., 30 c. c., and 20 c. c. successive quantities of hot water. The combined filtrations are evaporated just to dryness in a tared dish and left in a vacuum desiccator overnight. Rinse the residue two or three times with CP ether. Dry on top of the oven to remove ether vapors, cool and weigh, residue equaling ammonium nitrate present in the sample.

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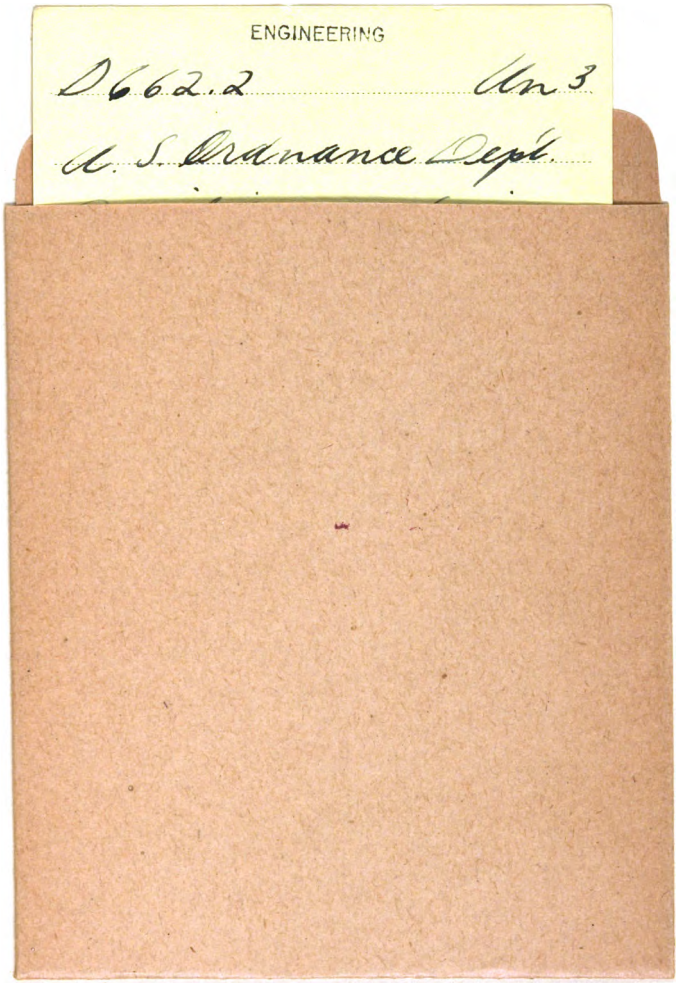

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